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ANALYTICAL REFERENCE SERVICE TRAINING PROGRAM. SAMPLE TYPE IA, WATER-MINERALS

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

November 1958

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November 1958

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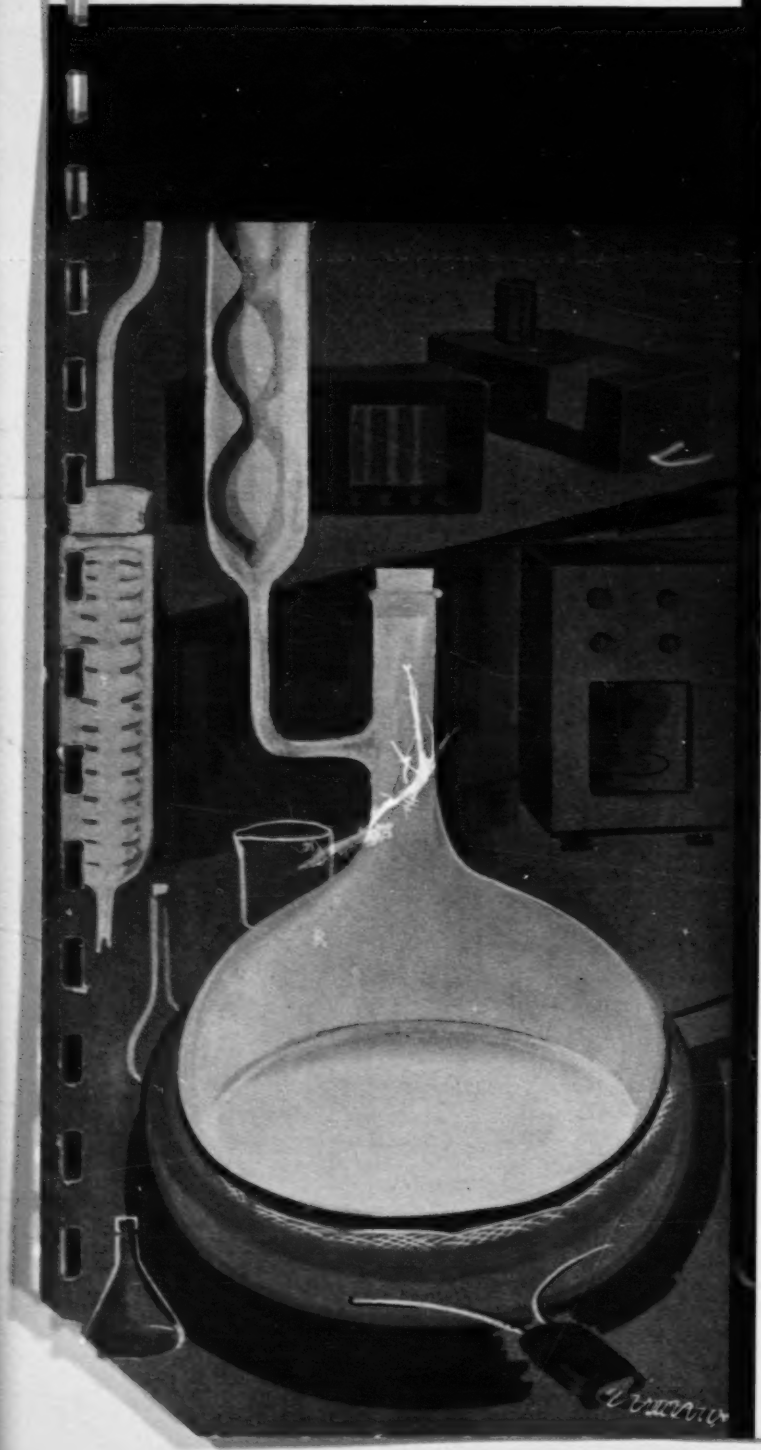

training program

Robert A. Taft

Sanitary Engineering Center

Cincinnati, Ohio

U. S. Department of Health, Education, and Welfare

· Public Health Service

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ANALYTICAL REFERENCE SERVICE

INTRODUCTION

The Analytical Reference Service conducted by the Sanitary Engineering Center has as its primary goal the evaluation of laboratory methods in the field of sanitary engineering. The Reference Service itself is a voluntary association of member organizations responsible for the conduct of laboratory programs. The evaluations are obtained by the cooperative efforts of the members in the analysis of identical samples.

This mechanism provides:

1. A statistical evaluation of procedures, including precision and accuracy.

2. An opportunity for a participant to compare his laboratory procedures and results with other laboratories having similar responsibilities.

3. An exchange of information regarding weaknesses of currently approved methods.

4. Evidence regarding methods requiring further development or perhaps entirely new approaches.

5. A framework for broad-scale evaluation of new analytical methods.

PLAN OF OPERATION

Initially, efforts are being directed toward the chemical examination of water. The scope of the program will be broadened gradually to include other types of examinations and other media.

Using the most refined grade of chemicals available, samples are prepared containing measured amounts of the desired constituent. Decisions as to the qualitative makeup of any particular sample follow suggestions from the members and from the staff of the Sanitary Engineering Center.

After a sample is designed and prepared, a notice announcing its availability and qualitative makeup is sent with a self-addressed reply card to member organizations. An affirmative reply initiates immediate shipment of a portion of the described sample. Results are requested within some reasonable period, usually sixty days.

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REPORTING OF RESULTS AND COMMENTS

Data are returned to the Sanitary Engineering Center on forms supplied with the sample. Space is provided on the forms for numerical values and a narrative critique of analytical procedures used.

The results obtained by the cooperating laboratories are compiled as in the accompanying report. From examination of the combined data it is hoped that reliable estimates may be made of the accuracy and precision of the methods employed.

All laboratories are strongly encouraged to supply comments on the analytical methods they use. A complete log of pertinent details, including difficulties, modifications, sources of error, and other factors, is extremely valuable. Such a compilation of comments represents an exchange of ideas and opinions that is a significant part of the final report.

H. P. Kramer

H. P. Kramer
Chief, Training Program

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ANALYTICAL REFERENCE SERVICE

MEMBERS AS OF AUGUST 1, 1958

State Agencies

Arizona State Department of Health
Arkansas State Board of Health
California Department of Water Resources (Sacramento)
California Department of Water Resources (San Bernardino)
California Department of Water Resources (Riverside)
California State Department of Health (Berkeley)
California State Department of Health (Los Angeles)
Colorado State Department of Public Health
Connecticut State Department of Health
Florida State Board of Health
Territory of Hawaii Department of Health
Idaho State Board of Health
Illinois State Water Survey Division
Kentucky State Department of Public Health
Louisiana State Department of Health
Maryland State Department of Health
Maryland Water Pollution Control Commission
Michigan State Department of Health
Minnesota State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
Nebraska State Department of Health
New Hampshire Water Pollution Commission
New Jersey State Department of Health
New Mexico State Department of Public Health
New York State Conservation Department
New York State Department of Health
North Carolina State Stream Sanitation Committee
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania State Department of Health
South Carolina State Water Pollution Control Authority
South Dakota State Board of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont Department of Health
Vermont Water Conservation Board
Virginia Water Control Board
Washington State Department of Health
West Virginia State Water Commission

Municipal Agencies

City of Los Angeles Department of Water and Power
Chicago Department of Water and Sewers

Federal Agencies

Army Chemical Center, Edgewood, Maryland
Sanitary Engineering Division, 13th Naval District
U.S. Geological Survey, Department of the Interior
Columbus, Ohio
Sacramento, California
Washington, D. C.

Universities

Rutgers University, Department of Sanitation
Purdue University, Department of Chemistry
Georgia Tech, Department of Applied Biology
University of Pittsburgh, Graduate School of Public Health

Industrial

National Aluminate Corporation

PARTICIPANTS IN THIS STUDY OF SAMPLE TYPE 1-A

(Distributed January, 1958)

Arizona State Department of Health
Arkansas State Board of Health
California State Department of Health (Berkeley)
California State Department of Health (Los Angeles)
Illinois State Water Survey Division
Kentucky State Department of Public Health
Louisiana State Department of Health
Maryland State Department of Health
Michigan State Department of Health
Minnesota Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
Nebraska State Department of Health
New Hampshire Water Pollution Commission
New Jersey State Department of Health
New Mexico State Department of Public Health
New York State Conservation Department
New York State Department of Health
North Carolina State Stream Sanitation Commission
Ohio State Department of Health
Pennsylvania State Department of Health
South Dakota State Board of Health
Tennessee State Department of Public Health
Texas State Department of Health
Utah State Department of Health
Vermont Department of Health
Vermont Water Conservation Board
Army Chemical Center, Edgewood, Maryland
Rutgers University, Department of Sanitation
U.S. Geological Survey, Department of the Interior
Raleigh, North Carolina
Sacramento, California

SUMMARY OF ANALYTICAL REFERENCE SAMPLES WHICH HAVE BEEN DISTRIBUTED AND ON WHICH REPORTS HAVE BEEN COMPLETED

SAMPLE TYPE I

(Mineral, Water) to be analyzed for calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium.

SAMPLE TYPE II

(Heavy Metals, Water) to be analyzed for copper, cadmium, aluminum, chromium, iron, lead, manganese, and zinc.

SAMPLE TYPE III

(Fluoride, Water) to be analyzed for fluoride in the presence and absence of interferences with and without distillation, using a specified procedure.

SAMPLES WHICH HAVE BEEN DISTRIBUTED AND WHICH ARE NOW IN THE PROCESS OF STUDY

SAMPLE TYPE IV

(Inorganic Particulate, Air) to be analyzed for sulfate, chloride, fluoride and nitrate.

SAMPLE TYPE V

(Radiological, Water) to be processed and counted for measurement of gross beta activity.

REPORT ON SAMPLE TYPE I-A

Purpose of this Study

Sample Type I-A has the same composition as the original sample Type I and has been offered at the request of a number of the Analytical Reference Service members. Observations on the results of the Type I sample suggested that certain techniques were superior in their application to specific determinations. For example, the electrometric endpoint for alkalinity measurements and chloride correction for nitrate determinations were strongly indicated. Further details regarding the results and their interpretations on Sample Type I-A are discussed in the appropriate sections of this report. In addition, the determinations performed on this sample serve as a yardstick of laboratory competency and consequently may be used both as a method of training new personnel and as a basis for judgment of laboratory efficiency.

Preparation of Sample

Substrate:

Distilled water passed through a de-ionizing column

Chemicals:

All reagents were ACS reagent grade taken from freshly opened bottles.

Composition:

Sample Type I-A consisted of 180 liters of substrate containing carefully measured portions of calcium sulfate, magnesium chloride, sodium nitrite, potassium nitrate and sodium bicarbonate to give the following concentrations:

Calcium	120 mg/l	Alkalinity (as $CaCO_3$)	17 mg/l
Magnesium	75	Nitrite Nitrogen	0.20
Total Hardness (as $CaCO_3$)	608	Nitrate Nitrogen	1.3
Sulfate	288	Sodium	8
Chloride	219	Potassium	3.6

Repeated analyses in this laboratory do not show any loss of nitrite or nitrate nitrogen or any gain or loss of alkalinity.

Significance of the Statistics:

In this study, 31 laboratories participated and reported a total of 316 analytical results based upon measurements in triplicate.

For purposes of convenience, the average value of each determination as reported is tabulated along with the deviation from the amount added. The significance of these statistics have been previously discussed (Report on Sample Type II, July 1957).

The standard deviations were calculated by using the difference between the reported averages and the amount of material actually added. All reported values greater than two standard deviations were then eliminated and the standard deviation recalculated. This "refined" standard deviation more nearly reflects the accuracy of the analytical methods used in the study since approximately 95% of the data is retained but discards gross errors stemming from incorrect dilution factors, etc.

It should be remembered that the standard deviations reported here are a function of concentration. If the amount of material being measured would be halved or doubled, it is probable that the standard deviation would vary depending upon whatever changes would be required or affected by the new concentration.

In order that the accuracy of the methods be more directly related to the laboratories performing the determinations, the term "50% Range" is again used (Report on Sample Type II, July 1957). The figure is defined as the maximum deviation from the amount added for the better half (50%) of all results for each measurement. For example, on the calcium determination, the range for 31 laboratories was 83 mg/l, but 16 (50%) laboratories reported values within 2 mg/l of the true figure. The 2 mg/l represents the range within which most of the results will fall. Conversely, any laboratory whose results do not differ from the amount added by more than the 50% range has performed as well, or better than half of the participants for that particular determination.

CALCIUM

For the calcium measurement, six different procedures were used by the cooperating groups. Twenty laboratories used some modification of the EDTA titration, five used the permanganate titration and the remaining groups used variously gravimetric, soap, flame and calculation procedures. In general, all methods gave excellent results, the average deviation for 33 reported results being only 5.4 mg/l and a standard deviation of 5.5 mg/l. These figures indicate that at a concentration of 120 mg/l, it is possible to come within 5% of the true value regardless of method used.

For the EDTA procedures, the standard deviation was 4.2 mg/l (within 4%) and the volumetric permanganate method had a standard deviation of only 2.1 mg/l (within 2%). While the latter method appears to give better results, it would seem that the EDTA titrations would be strongly recommended on the basis of simplicity and speed.

SUMMARY:

Amount Added	120 mg/l
Average Deviation from Amount Added	5.4 mg/l
Standard Deviation from Amount Added	5.5 mg/l
50% Range	2.0 mg/l
Method Most Commonly Used	EDTA
Method Preferred	EDTA
Total Number of Observations	33

CALCIUM

Amount Added = 120 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	120 121 122	121	0.54	0.83	Gravimetric Std. Methods, 10th Edition
1	117 120 119	119	0.84	1.11	EDTA
2	121 --- ---	121	0.00	0.83	EDTA
3	122 122 124	123	0.81	2.23	EDTA
4	123 124 122	123	0.54	2.50	EDTA
5	127 123 124	125	1.34	3.89	Calculated
6	120 120 120	120	0.00	0.00	EDTA Std. Methods
7	118 118 118	118	0.00	1.67	EDTA
8	132 131 ---	132	0.38	9.60	Gravimetric
9	120 120 121	120	0.28	0.28	EDTA
10	119 121 121	120	0.83	0.83	Gravimetric Std. Methods, 10th Edition

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	121 122 120	121	0.55	0.83	Volumetric Permanganate Std. Methods, 10th Edition
12	124 122 120	122	1.09	1.67	EDTA Std. Methods
13	123 120 121	121	0.83	1.11	EDTA
14	121 121 ---	121	0.00	0.83	EDTA
15	114 114 ---	114	0.00	5.00	EDTA
16	115 109 ---	112	2.68	6.67	Soap Titration Std. Methods
17	123 123 123	123	0.00	2.50	Volumetric Permanganate
18	114 115 114	114	0.29	4.73	EDTA
19	121 123 ---	122	0.82	1.67	Volumetric Permanganate
19A	124 --- ---	124	---	3.34	Flame
20	125 125 ---	125	0.00	4.16	EDTA Std. Methods, 10th Edition
21	119 121 123	121	1.10	1.39	EDTA

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
22	120 117 ---	118	1.27	1.25	EDTA
23	124 124 122	123	0.81	2.78	EDTA
24	125 121 121	122	1.37	1.94	Volumetric Permanganate Std. Methods, 10th Edition
24A	119 117 ---	118	0.85	1.67	Volumetric Permanganate Std. Methods, 10th Edition
25	131 --- ---	131	---	9.17	Gravimetric
26	118 118 117	118	0.28	1.94	EDTA
27	135 --- ---	135	---	12.50	EDTA
28	135 136 132	134	1.25	11.95	EDTA
29	117 116 116	116	0.28	3.06	EDTA Std. Methods, 10th Edition
30	120 --- ---	120	---	0.00	EDTA Std. Methods, 10th Edition
31	53 52 --	52	0.96	56.00	Flame

Avg. of the means 119
Mean % deviation within labs 0.66
Mean % deviation from amt. added..... 4.70

COMMENTS ON CALCIUM METHOD

Lab. 1	We prefer the Betz and Noll method to the Standard Methods procedures because of its simplicity and because it does not involve the separation of calcium by precipitation and filtration. Method appears to be sufficiently accurate for routine analyses.	EDTA, JAWWA 42:49(1950)
Lab. 2	No comments.	EDTA
Lab. 3	Versenate (murexide) method seems very good and is rapid for routine work.	EDTA
Lab. 4	The Versenate was standardized against a standard calcium solution containing an equal amount of magnesium, to adjust for any coprecipitation which might occur under actual conditions of analysis.	EDTA
Lab. 5	No comments.	CALCULATED
Lab. 6	No comments.	EDTA, STD. METH.
Lab. 7	Using the indicator made according to method given in the reference (Industrial & Engineering Chemistry, Analytical Edition, Vol. 28, No. 6, pp. 1027) we are getting very good results. It seems to be far superior to the murexide or calcein procedure.	EDTA, ANAL. CHEM. 28:1027 (1956)
Lab. 8	Time consuming, but checks well. Not a routine analysis.	GRAVIMETRIC
Lab. 9	Time is quite an element in the work here as I have the entire State's water supplies to analyze. I do not think that the Versenate method is more accurate than the potassium permanganate method but it is a great time saver and seems to be sufficiently accurate for all practical purposes. Calcium hardness divided by 2.497 gives the milligrams per liter of calcium. All public supplies are filtered before determination is made.	EDTA
Lab. 10	No comments.	GRAVIMETRIC, STD. METH. 10th ED.
Lab. 11	The precision obtained and accuracies experienced in the past on controls justify the use of the time consuming permanganate volumetric method.	VOL. PERMANGANATE, STD. METH. 10th ED.
Lab. 12	EDTA titration at pH 12-13. Commercial product used as endpoint indicator. Practice is needed to detect endpoint.	EDTA, STD. METH.

COMMENTS ON CALCIUM METHOD

Lab. 13 — No comments. — EDTA

Lab. 14 — The only difficulty encountered with this method when applied directly to water samples was that the endpoint was unstable, the blue color changing to a purple on standing for a short time. This was not encountered when mixtures of standard solutions of $CaCl_2$ and $MgSO_4$ were titrated. The difficulty was partly overcome by first acidifying samples with HCl, and boiling to remove CO_2. The method is rapid, and does not require difficult manipulation. Replicate titrations of standard $CaCl_2$ solution have agreed to within 0.2%; no data is on hand as to accuracy and precision when used on water samples. Method previously used was the EDTA titration with screened murexide. Results have been about 1/2% lower than $KMnO_4$ titration via CaC_2O_4. Murexide endpoint difficult to detect.

EDTA, ANAL. CHEM.29:259 (1957)

Lab. 15 — Calcium was determined by the Versenate procedure. — EDTA

Lab. 16 — Convenient and of sufficient accuracy for the evaluation of potable water from the point of view of public health.

SOAP TITRATION, STD. METH.

Lab. 17 — No comments. — VOL. PERMANGANATE

Lab. 18 — This method is quick and as far as we have been able to determine, gives satisfactory accuracy.

EDTA

Lab. 19 — Permanganate method. No particular difficulty experienced with procedure, but it is subject to various interferences. The precision and accuracy are good but the method is time consuming. Flame photometric method. Sulfate ion is chief interference, but this is removed completely by passing sample through an ion exchange resin (Rohm & Haas IR-401). Background interference is low. The method is rapid and manipulation is simple. We believe the precision and accuracy are excellent.

VOL. PERMANGANATE AND FLAME

Lab. 20 — Complexometric method satisfactory.

EDTA, STD. METH. 10th ED.

Lab. 21 — With Versene, titration method gave low results until a factor of 1.04 was used. Titrations gave only 96% recovery on standard calcium solution.

EDTA

Lab. 22 — No comments. — EDTA

Lab. 23 — Rapid, method accurate enough for routine purposes. Endpoint not as dramatic as in the hardness test.

EDTA

COMMENTS ON CALCIUM METHOD

Lab. 24 — The amount of ammonium oxalate solution recommended in Standard Methods, 10th ED., is excessive and interferes if the filtrate from the calcium determination is used for determination of magnesium using a Versene titration. We use 5 ml of saturated ammonium oxalate and find this adequate.

VOL. PERMANGANATE, STD. METH. 10th ED.

Lab. 25 — No comments. GRAVIMETRIC

Lab. 26 — Calcium is determined by titrating the sample with a standard solution of EDTA using murexide as the calcium color indicator. No difficulties were encountered in analyzing for calcium in the sample submitted by the USPHS. This complexiметric method for the determination of calcium affects a considerable saving in time when compared with the volumetric permanganate method. The method requires a smaller amount of technical detail while affording about the same precision and accuracy as other methods. Large quantities of natural color in waters tend to mask the endpoint, giving a positive error to the analysis. A good method for the removal of color would be an aid in the determination.

EDTA

Lab. 27 — This result was obtained by difference between the total hardness of the sample and the "total hardness" found after removal of the calcium oxalate. See magnesium method below.

EDTA

Lab. 28 — No comments. EDTA

Lab. 29 — Use Betz prepared solid indicator. Routine procedure.

EDTA, STD. METH. 10th ED.

Lab. 30 — No comments. EDTA, STD. METH. 10th ED.

Lab. 31 — Run using calcium buffer as per West, Folse & Montgomery; Anal. Chem. 22, No. 5, 1950.

FLAME

MAGNESIUM

As in the calcium measurement, magnesium is determined in a variety of ways. Since hardness and calcium were also run, 12 groups took advantage of numerical relationships and reported magnesium by calculation. Other methods used included EDTA titration, soap titration, gravimetric, colorimetric, flame and lime water. The average deviation for all methods was only 3.3 mg/l and standard deviation of 2.7 mg/l.

For the actual manipulative procedures, the EDTA methods gave a standard deviation of 1.6 mg/l. The calculated magnesium results had a standard deviation of 5.4 (based on 12 results) which was not as good as the other 2 methods. It must be remembered that errors, however small, in the calcium and hardness measurements are reflected and magnified in the calculation.

In summary, the three most commonly used methods for magnesium all give excellent results. When it becomes necessary to actually carry out the determination, the EDTA titration would be preferred on the basis of speed and simplicity even though the gravimetric procedure appears to be slightly more accurate.

SUMMARY:

Amount Added	75 mg/l
Average Deviation from Amount Added	3.3 mg/l
Standard Deviation	2.7 mg/l
50% Range	2.0 mg/l
Method Most Commonly Used	EDTA
Method Preferred	EDTA
Total Number of Observations	32

MAGNESIUM

Amount Added = 75 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	73 74 75	74	0.88	1.33	Gravimetric Std. Methods, 10th Edition
1	80 81 80	80	0.41	7.11	EDTA
2	74 -- --	74	---	1.33	EDTA
3	78 78 81	79	1.68	5.33	Calculated
4	75 -- --	75	---	0.00	Calculated
5	72 72 --	72	0.00	4.00	Lime Water
6	74 80 78	77	3.03	4.00	Titan Yellow Sandell
7	78 78 78	78	0.00	4.00	Calculated
8	74 74 --	74	0.00	1.33	Gravimetric
9	77 77 76	77	0.43	2.23	Calculated
10	76 75 76	76	0.44	0.89	Gravimetric Std. Methods, 10th Edition

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	76 81 77	78	2.56	4.00	Gravimetric Std. Methods, 10th Edition
12	75 75 75	75	0.00	0.00	Gravimetric Std. Methods
13	72 76 74	74	1.80	2.26	Calculated
14	80 -- --	80	---	6.67	Calculated
15	78 78 --	78	0.00	4.00	Calculated
16	85 83 --	84	1.19	12.00	Soap Titration Std. Methods
17	77 77 76	77	0.43	2.23	Gravimetric
18	81 -- --	81	---	8.00	Calculated
19	76 -- --	76	---	1.33	Flame Photometric
20	80 75 --	77	3.25	3.34	EDTA
21	75 74 73	74	0.91	1.33	Calculated
22	79 82 --	80	1.88	7.34	Calculated

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
23	65 -- --	65	---	13.32	Calculated
24	76 76 75	76	0.44	0.89	EDTA
24A	75 76 --	76	0.66	0.67	EDTA
25	75 -- --	75	---	0.00	Gravimetric
26	80 81 81	81	0.41	7.56	Calculated
27	69 68 69	69	0.48	8.45	EDTA
28	72 71 71	71	0.47	4.90	Calculated
29	73 73 74	73	0.45	2.23	Calculated
30	84 -- --	84	---	1.20	Calculated
31	82 82 --	82	0.00	9.33	Flame Photometry

Avg. of the means 76
Mean % deviation within labs 0.83
Mean % deviation from amount added..... 4.03

COMMENTS ON MAGNESIUM METHOD

Lab. 1 As under calcium. Have not had opportunity to try Brilliant Yellow method.

EDTA, BETZ & NOLL. JAWWA 42:49. 1950

Lab. 2 No comments.

EDTA

Lab. 3 The method of calculation is done by computing the difference between the total hardness and the calcium or calcium carbonate. We find the method very satisfactory because the total hardness and calcium titrations are rapid and satisfactory for routine work.

CALCULATED

Lab. 4 The average value for calcium as calcium carbonate was subtracted from the average value for total hardness and the result converted to magnesium.

CALCULATED

Lab. 5 The "lime water method" was used here. Sample neutralized, boiled, cooled, taken to pH 8.3, definite volume of lime water added, made to volume, settled, and definite volume titrated with N/50 acid to pH of 8.3.

LIME WATER

Lab. 6 No comments.

TITAN YELLOW, SANDELL

Lab. 7 The accuracy depends upon the results of the calcium and hardness titration as it is calculated by difference. It appears to give acceptable results.

CALCULATED

Lab. 8 Very time consuming, but apparently precise. Not a routine analysis.

GRAVIMETRIC

Lab. 9 The calculated method is as accurate as the Versenate method for total calcium and magnesium hardness and the calcium hardness as determined by the Versenate method using CalVer I. as the indicator. This method seems to be sufficiently accurate for all practical purposes and ia a great time saver. Magnesium hardness divided by 4.115 gives the milligrams per liter of magnesium.

CALCULATED

Lab. 10 No comments.

GRAVIMETRIC, STD. METH. 10th ED.

Lab. 11 Requests for this determination are usually made with those for calcium, which makes it convenient to use the filtrate from the latter. Comments made on the method for calcium are also applicable here. The Titan Yellow colorimetric and the oxime methods have been used occasionally with good results.

GRAVIMETRIC, STD. METH. 10th ED.

Lab. 12 Gravimetric pyrophosphate method is many times substituted by calculating magnesium by difference of EDTA hardness and EDTA calcium determinations since our laboratory data indicates this calculation is valid for the great majority of samples.

GRAVIMETRIC, STD. METH.

COMMENTS ON MAGNESIUM METHOD

Lab. 13	No comments.	CALCULATED
Lab. 14	See comments on total hardness method.	CALCULATED
Lab. 15	Magnesium was computed from data secured by using the total hardness and the calcium results.	CALCULATED
Lab. 16	Convenient and of sufficient accuracy for the evaluation of potable water from the point of view of public health.	SOAP TITRATION, STD. METH.
Lab. 17	No comments.	GRAVIMETRIC
Lab. 18	We have not attempted to run magnesium directly. Calculated by difference between total hardness and calcium.	CALCULATED
Lab. 19	The sensitivity of the magnesium flame is weak and highly subject to background interference. When using acetylene as the fuel in the flame photometric method, it is desirable to concentrate the sample 4-8 times and compare with standards containing approximately the same amounts of calcium and sodium as the sample. When these compensations are made, this method compares favorably with other methods with respect to accuracy and speed.	FLAME PHOTOMETRIC
Lab. 20	Complexiметric method satisfactory.	EDTA
Lab. 21	Results reported are based on corrected calcium figures.	CALCULATED
Lab. 22	No comments.	CALCULATED
Lab. 23	No comments.	CALCULATED
Lab. 24	Using Univer I indicator and Versenate titration on the filtrate from the calcium determination, some people in the laboratory experience difficulty in recognizing the endpoint. A sharper endpoint would be desirable.	EDTA
Lab. 25	No comments.	GRAVIMETRIC
Lab. 26	Magnesium is not determined directly but is calculated as the equivalent difference between the total titrated polyvalent cations minus the calcium value. This by-difference method for the determination for magnesium is felt to be precise and accurate in the absence of polyvalent cations other than calcium. (See comments on total hardness).	CALCULATED

COMMENTS ON MAGNESIUM METHOD

Lab. 27	This result was obtained by precipitation the calcium as calcium oxalate in an alkaline condition and running total hardness on the filtrate.	EDTA
Lab. 28	No comments.	CALCULATED
Lab. 29	Determined by difference. Total hardness - calcium hardness.	CALCULATED
Lab. 30	No comments.	CALCULATED
Lab. 31	Ibid. High background response.	FLAME PHOTOMETRY

HARDNESS

Thirty-four results were reported for the hardness determination, of which 31 were obtained by the EDTA titration. The average deviation of only 13 mg/l at a level of 600 mg/l indicates that the method gives excellent results over a wide range of concentrations. Materials which are said to interfere with this procedure such as iron, aluminum, manganese or polyphosphates were not present in the sample so that the accuracy predicted here may be better than that obtained on natural samples. However, probably the commonest source of error in this operation is aging of Chrome Black T indicator solution. This would probably occur in laboratories where hardness determinations are not done on a routine basis.

The standard deviation of 13.7 mg/l indicates a reliable method.

SUMMARY:

Amount Added	608 mg/l (as $CaCO_3$)
Average Deviation from Amount Added	13 mg/l
Standard Deviation	13.7 mg/l
50% Range	10 mg/l
Method Most Commonly Used	EDTA with Eriochrome Black T
Method Preferred	Same
Total Number of Observations	34

HARDNESS AS $CaCO_3$

Amount Added = 608 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	593 593 593	593	0.00	2.46	EDTA Ammonia Buffer
1	652 654 658	655	0.36	7.68	EDTA Ammonia Buffer
2	605 610 ---	608	0.41	0.41	EDTA
3	624 624 645	631	1.48	3.78	EDTA
4	617 618 ---	618	0.05	1.56	EDTA
5	604 605 ---	604	0.05	0.58	EDTA
6	613 615 611	613	0.22	0.82	EDTA Borate Buffer
7	616 616 614	615	0.16	1.20	EDTA Ammonia Buffer
8	605 605 ---	605	0.00	0.49	EDTA
9	616 616 616	616	0.00	1.32	EDTA
10	610 610 602	607	0.61	0.55	Soap Titration Std. Methods 10th Edition

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	602 604 604	603	0.17	0.77	EDTA Ammonia Buffer
12	614 614 616	615	0.16	1.07	EDTA Ammonia Buffer
13	602 613 607	607	0.16	0.66	EDTA
14	634 628 ---	631	0.48	3.78	EDTA
15	613 613 ---	613	0.00	0.82	EDTA Ammonia Buffer
16	583 561 ---	572	1.92	5.92	Std. Methods
17	624 626 622	624	0.32	2.63	EDTA Ammonia Buffer
17A	630 630 630	630	0.00	3.62	Calculated
18	616 616 620	617	0.27	1.54	EDTA
19	619 --- ---	619	---	1.81	EDTA
19A	622 --- ---	622	---	2.31	Calculated from Flame Photometry
20	640 620 ---	630	1.59	3.62	EDTA

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
21	610 600 605	605	0.55	0.71	EDTA
22	625 628 ---	626	0.24	3.04	EDTA
23	580 580 600	587	1.54	3.51	EDTA
24	609 612 610	610	0.16	0.38	EDTA
24A	604 --- ---	604	---	0.66	EDTA
25	604 --- ---	604	---	0.66	
26	625 628 625	626	0.22	2.96	EDTA
27	616 620 620	619	0.27	1.76	EDTA
28	625 633 630	629	0.48	3.51	EDTA
29	592 590 594	592	0.23	2.63	EDTA
30	592 --- ---	592	---	2.63	EDTA Ammonia Buffer
31	636 636 ---	636	0.00	4.60	EDTA Borate Buffer

Avg of the means 614
Mean % deviation within labs 0.42
Mean % deviation from amt. added..... 2.16

COMMENTS ON TOTAL HARDNESS METHOD

Lab. 1	Method satisfactory.	EDTA, AMMONIA BUFFER, STD. METH.
Lab. 2	No comments.	EDTA
Lab. 3	Versenate (Eriochrome Black T) is very rapid and very good for routine work. Endpoint is slow in developing.	EDTA
Lab. 4	No comments.	EDTA
Lab. 5	We use the EDTA titration method, adding a dry NaCN-indicator buffer mixture. Found danger of over titration. The endpoint must be approached slowly. The discharge of the last trace of pink can be detected on a spectrophotometer at 540 millimicrons.	EDTA, MODIFIED
Lab. 6	No comments.	EDTA, BORATE BUFFER, STD. METH.
Lab. 7	This is the standard Versenate titration and appears to give very good results with a clear endpoint.	EDTA, AMMONIA BUFFER
Lab. 8	Simple and accurate.	EDTA
Lab. 9	Total hardness was determined by the Versenate method using Univer I as the indicator. This indicator contains the buffer and alkali to raise the pH to give the best results.	EDTA, UNIVER-I
Lab. 10	No comments.	SOAP TITRATION, STD. METH. 10th ED.
Lab. 11	The ammonia buffer method is preferred to the borate technique since use of the former results in a sharper endpoint and the indicator appears to have greater stability. Good precision and accuracy have been experienced.	EDTA, AMMONIA BUFFER, STD. METH. 10th ED.
Lab. 12	Ammonia buffer method used. Titration with EDTA performed at pH 10.	EDTA, AMMONIA BUFFER
Lab. 13	No comments.	EDTA
Lab. 14	No unusual difficulties. Method is rapid, and agrees within 1% of the results obtained for calcium by the $KMnO_4$ titration and for magnesium by weighing as $Mg_2P_2O_7$.	EDTA
Lab. 15	Total hardness was determined by the Versenate method employing the use of the ammonia buffer and NaCN as the inhibitor.	EDTA, AMMONIA BUFFER

COMMENTS ON TOTAL HARDNESS METHOD

Lab. 16 — Convenient and sufficiently accurate for the evaluation of potable water from the point of view of public health.

STD. METH.

Lab. 17 — The ammonia buffer procedure is used for Versenate hardness. Samples are titrated without delay after the addition of the buffer and other reagents.

EDTA, AMMONIA BUFFER AND CALCULATED

Lab. 18 — Same as for calcium method. Indicator must be watched as it gives erratic results on aging.

EDTA

Lab. 19 — We find this to be an excellent method, very superior to the old soap titration method. If there is a deficiency in the procedure, it appears to be the relatively high degree of instability of the borate buffer mixture. The method is rapid, easy to perform, and the precision and accuracy are good.

EDTA AND CALCULATION FROM FLAME PHOTOMETRY

Lab. 20 — Less time consuming and more precise than soap method.

EDTA

Lab. 21 — The Versene method always gives 100% recovery on standard samples.

EDTA

Lab. 22 — No comments.

EDTA

Lab. 23 — Satisfactory results - very sharp endpoint. EDTA, UNIVER.

Lab. 24 — No comments.

EDTA, UNIVER 1.

Lab. 25 — No comments.

Lab. 26 — The total hardness due to the polyvalent cations in solution is determined by titration with a standard EDTA solution using Eriochrome Black T as an indicator. This method gives accurate and precise results if proper measures are taken to eliminate interfering substances. Hydroxlamine hydrochloride and sodium cyanide are used to eliminate interferences caused by heavy metals and higher valence ions. Highly colored samples will give a different colored endpoint (green) from samples having no color, but the color does not seem to interfere with the accuracy or precision of the method.

EDTA

Lab. 27 — Method is accurate and simple except where strongly colored solutions make endpoint difficult to determine. In very few cases is it necessary to do more than dilute the sample in order to get rid of interferences.

EDTA

Lab. 28 — No comments.

EDTA, BETZ

COMMENTS ON TOTAL HARDNESS METHOD

Lab. 29 50 ml sample - Indicator - Eriochrome Black T in Triethanolamine.

EDTA, STD. METH. 10th ED.

Lab. 30 No comments.

EDTA, AMMONIA BUFFER, STD. METH. 10th ED.

Lab. 31 Analysis run 4/18/58.

EDTA, BORATE BUFFER

SULFATE - 288 mg/l

All of the classical techniques used in quantitative analyses, gravimetric, volumetric, photometric, are employed in the sulfate determination, but the gravimetric procedure still remains the most commonly used. Thirty-eight results were reported, the methods used numbering 22 gravimetric, 11 turbidimetric, 4 volumetric and 1 calculated.

The arithmetic mean for all methods was 283 mg/l with an average deviation of 14.4 mg/l and a standard deviation of 10.1 mg/l.

The standard deviations for the gravimetric and turbidimetric methods were 9.2 and 32.1 mg/l, respectively. Since the speed and simplicity of the turbidimetric procedure is offset by its lack of accuracy, it would be advisable for a laboratory to determine the degree of accuracy required before choosing a method for routine use.

SUMMARY:

Amount Added	288 mg/l
Average Deviation from Amount Added	14.1 mg/l
Standard Deviation	10.1 mg/l
50% Range	7 mg/l
Method Most Commonly Used	Gravimetric
Method Preferred	Gravimetric
Total Number of Observations	38

SULFATE

Amount Added = 288 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	290 292 295	292	0.57	1.50	Gravimetric Std. Methods
1	317 317 322	319	0.73	1.07	Titrimetric Std. Methods
2	290 --- ---	290	---	0.70	Gravimetric
3	278 265 248	264	3.91	8.45	Gravimetric
4	278* 286 280	281	0.78	2.50	Turbidimetric *5 Replicates run
5	298 302 ---	300	0.67	4.17	Turbidimetric Std. Methods
6	245 246 245	245	0.14	14.81	Std. Methods
7	288 288 288	288	0.00	0.00	Gravimetric Std. Methods, 10th Edition
8	274 275 280	276	0.85	4.06	Gravimetric
9	296 290 297	295	0.79	2.20	Gravimetric Std. Methods
10	286 288 286	287	0.35	0.46	Gravimetric Std. Methods

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	298 298 298	298	0.00	3.47	Turbidimetric Std. Methods, 10th Edition
12	288 291 296	292	0.86	1.22	Gravimetric
13	304 300 302	302	0.44	4.86	Gravimetric
14	285 280 ---	282	0.89	1.91	Gravimetric
15	290 295 ---	292	0.86	1.56	Turbidimetric
15A	297 --- ---	297	---	3.12	Gravimetric
15B	299 296 ---	298	0.50	3.30	Own
16	192 188 ---	190	1.05	0.70	Turbidimetric Std. Methods
17	292 292 293	292	1.13	1.50	Gravimetric
18	269 280 275	275	1.33	4.64	Gravimetric
18A	281 290 285	285	1.05	1.39	Potassium Rhodizonate
19	291 --- ---	291	---	1.04	Gravimetric

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
19A	292 --- ---	292	---	1.39	Chromate Substitution
19B	297 --- ---	297	---	3.12	Calculated
20	285 287 ---	286	0.35	0.70	Gravimetric
21	298 294 300	297	0.79	3.01	Turbidimetric
22	290 294 ---	292	0.69	1.39	EDTA
23	290 290 300	293	1.48	1.85	Turbidimetric
24	287 281 287	285	0.94	1.04	Gravimetric Std. Methods, 10th Edition
24A	284 286 ---	285	0.35	1.04	Gravimetric Std. Methods, 10th Edition
25	275 --- ---	275	---	4.50	Gravimetric
26	282 282 ---	282	0.00	2.08	Gravimetric
26A	282 285 288	285	0.70	1.04	Turbidimetric
27	305 305 310	307	0.76	6.49	Gravimetric Std. Methods, 10th Edition

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
28	168 168 168	168	0.00	41.70	Turbidimetric
29	271 274 273	273	0.37	5.33	Gravimetric Std. Methods, 10th Edition
30	281 --- ---	281	---	2.43	Gravimetric Std. Methods, 10th Edition
31	275 280 ---	278	0.72	3.64	Turbidimetric

Avg. of the means 283
Mean % deviation within labs 0.75
Mean % deviation from amt. added..... 3.86

COMMENTS ON SULFATE METHOD

Lab. 1 Very difficult endpoint. Prefer turbidimetric methods in the absence of a suitable colorimetric procedure. Standard Methods turbidimetric procedure is too strict for routine laboratory use.

TITRIMETRIC, STD. METH.

Lab. 2 We use the turbidimetric method for sulfate determinations where the amount is about 150 ppm or less.

GRAVIMETRIC

Lab. 3 Turbidimetric method gives very good results with careful timing and stirring. This method is far better than either the gravimetric method or the titrimetric method using tetrahydroxyquinone indicator, when the sulfate content is very low. In cases where the sulfate content is very high, the gravimetric method seems to be the best method to use.

GRAVIMETRIC

Lab. 4 No comments. TURBIDIMETRIC

Lab. 5 We found no difficulty here. TURBIDIMETRIC, STD. METH.

Lab. 6 No comments.

Lab. 7 This is an old accepted procedure.

GRAVIMETRIC, STD. METH. 10th ED.

Lab. 8 Fairly simple, but time consuming. On routine analyses, in which the sulfate content is low, the turbidimetric method is used.

GRAVIMETRIC

Lab. 9 No comments. GRAVIMETRIC, STD. METH.

Lab. 10 No comments. GRAVIMETRIC, STD. METH. 10th ED.

Lab. 11 Most sulfate determinations are conducted in these laboratories by the turbidimetric method and good precision and accuracy have been demonstrated. The lengthy gravimetric method is employed when very high sulfate concentrations are involved.

TURBIDIMETRIC, STD. METH. 10th ED.

Lab. 12 Gravimetric method is still preferred method. Although it might be considered time consuming, in the long run it is method of choice since results are reliable and rarely need to be repeated.

GRAVIMETRIC

Lab. 13 $BaSO_4$ is filtered out with a Gooch crucible using a glass fiber filter and dried at 110°C. for about one hour.

GRAVIMETRIC

Lab. 14 No particular difficulties with most water samples.

GRAVIMETRIC

COMMENTS ON SULFATE METHOD

Lab. 15 Three methods of determining sulfates were used. The first two results were secured using the turbidimetric method with the wavelength of 350 on our spectrophotometer and a 1 minute stirring period preceding the final determination. The third listed result was made by gravimetric determination. The final 2 results were based upon a modified gravimetric method that we are working on but lack sufficient data to evaluate.

TURBIDIMETRIC - GRAVIMETRIC - OWN

Lab. 16 Convenient and of sufficient accuracy for the evaluation of potable water from the point of view of public health.

TURBIDIMETRIC, STD. METH.

Lab. 17 No comments.

GRAVIMETRIC

Lab. 18 We have found potassium rhodizonate to give better accuracy than THQ. We use mechanical stirrer and violet filter to mask yellow color of indicator.

GRAVIMETRIC - POTASSIUM RHODIZONATE

Lab. 19 Gravimetric Method. Time consuming, subject to various interferences; manipulation not difficult but somewhat tedious. If interferences are eliminated, the accuracy is good. Chromate Substitution Method. This method is in the experimental stage in our laboratory. It is subject to extreme control on pH and the use of rigorous buffers is essential. The method is fairly rapid when compared with most methods for sulfate and appears to have merit. Calculation from total milliequivalents. Obtained by balancing out total cation MEQ and total anion MEQ. Method is simple and apparently yields results comparable to those obtained by more conventional methods. Frequently used as a check method.

GRAVIMETRIC - CHROMATE SUBSTITUTION
CALCULATED FROM TOTAL MEQ

Lab. 20 Time consuming but not difficult. Gives most satisfactory results.

GRAVIMETRIC

Lab. 21 The turbidimetric method is modified by mixing glycerol with the salt-acid reagent in order to stabilize the precipitate of $BaSO_4$ and thus prevent flocculation.

TURBIDIMETRIC, MODIFIED

Lab. 22 No comments.

EDTA, SCHWARZENBACH

Lab. 23 Fine method for low concentrations. May run into dilution error in high samples.

TURBIDIMETRIC

Lab. 24 The gravimetric procedure is quite time consuming, but is the best method we know of. A good, rapid procedure would be highly desirable.

GRAVIMETRIC, STD. METH. 10th ED.

COMMENTS ON SULFATE METHOD

Lab. 25	No comments.	GRAVIMETRIC
Lab. 26	Sulfate was determined on the USPHS sample by both the standard gravimetric method which involves precipitation with barium chloride as barium sulfate and by a turbidimetric method which involves the controlled precipitation of the sulfate ion with sieved sized crystals of barium chloride in the presence of a high molar concentration of a hydrochloric acid-sodium chloride solution. The density of the suspension is determined with a Beckman Model B spectrophotometer. Both methods gave identical results for the sulfate ion concentration. No difficulties were encountered. The turbidimetric method is considered by this laboratory to yield accuracy and precision which is as good or better than the gravimetric method. Highly colored samples will give a positive error to the optical density readings obtained by the turbidimetric method which is approximately in proportion to the color of the sample. This difficulty may be corrected by determining the optical density of the colored sample which has been treated the same as the sample for the sulfate determination and subtracting this reading from the total optical density.	GRAVIMETRIC - TURBIDIMETRIC
Lab. 27	No comments.	GRAVIMETRIC, STD. METH. 10th ED.
Lab. 28	No comments.	TURBIDIMETRIC
Lab. 29	Results reported are gravimetric results. Routine method used in turbidimetric method (p. 197, B) 1:5 dilution of sample gave average results of 335 ppm.	GRAVIMETRIC, STD. METH. 10th ED.
Lab. 30	No comments.	GRAVIMETRIC, STD. METH. 10th ED.
Lab. 31	No comments.	TURBIDIMETRIC

CHLORIDE - 219 mg/l

On the chloride determination, 23 laboratories reported results based on the Mohr titration and six used the mercuric nitrate titration. One laboratory used an electrometric end point, employing silver nitrate as the titrant. For all methods, either grouped or separately, the accuracy was excellent. Some analysts commented that the Mohr end point was difficult to detect, but despite this failing, the results were good.

For the Mohr method, the arithmetic mean was 218 mg/l with a standard deviation of 6.2 mg/l. The mercuric nitrate gave slightly better results, an arithmetic mean of 216 mg/l and a standard deviation of 4.5. The mercuric nitrate figures however, are based on only six results.

SUMMARY:

Amount Added	219 mg/l
Average Deviation from Amount Added	4.0 mg/l
Standard Deviation	4.1 mg/l
50% Range	2.0 mg/l
Method Most Commonly Used	Mohr
Method Preferred	No choice
Total Number of Observations	31

CHLORIDE

Amount Added = 219 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	217 217 217	217	0.00	0.91	Mercuric Nitrate Std. Methods, 10th Edition
1	222 220 220	221	0.30	0.76	Mohr Std. Methods
2	215 --- ---	215	---	1.83	Mohr
3	219 219 215	218	0.77	0.61	Mohr
4	217 217 ---	217	0.00	0.91	Mohr
5	220 222 ---	221	0.45	0.91	Mohr
6	210 210 210	210	0.00	4.10	Mohr Std. Methods
7	220 220 220	220	0.00	0.45	Mohr Std. Methods, 10th Edition
8	213 214 ---	214	0.23	2.51	Mercuric Nitrate
9	225 225 225	225	0.00	2.74	Std. Methods
10	224 220 223	222	0.75	1.54	Mohr Std. Methods, 10th Edition

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	199 200 202	200	0.50	8.55	Mohr Std. Methods
12	218 220 220	219	0.33	0.46	Mercuric Nitrate Std. Methods
13	216 216 217	216	0.15	1.22	Mohr
14	227 227 ---	227	0.00	3.65	Mohr
15	220 220 ---	220	0.00	0.46	Electrometric
16	223 227 ---	225	0.89	2.74	Mohr Std. Methods
17	220 220 220	220	0.00	0.46	Mohr
18	218 220 220	219	0.46	0.46	Mohr
19	218 217 ---	218	0.23	0.69	Mohr
20	230 220 ---	225	2.22	2.74	Mohr
21	220 220 220	220	0.00	0.46	Mohr
22	222 222 ---	222	0.00	1.37	Mohr

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
23	215 205 215	212	2.04	3.34	Mercuric Nitrate Std. Methods, 10th Edition
24	220 220 221	220	0.15	0.61	Mercuric Nitrate Std. Methods, 10th Edition
24A	218 220 ---	219	0.46	0.46	Mercuric Nitrate Std. Methods, 10th Edition
25	210 --- ---	210	---	4.29	Mohr
26	215 218 220	217	0.92	0.91	Mohr
27	207 208 200	205	1.62	6.40	Mohr
28	420 420 414	418	0.64	90.90	Mohr
29	223 221 224	223	0.45	1.68	Mohr Std. Methods, 10th Edition
30	221 --- ---	221	---	0.91	Mohr Std. Methods, 10th Edition
31	221 221 ---	221	0.00	0.91	Mohr

Avg. of the means 218
Mean % deviation within labs 0.45
Mean % deviation from amt. added..... 4.57

COMMENTS ON CHLORIDE METHOD

Lab. 1	Method is satisfactory although considerable experience is required in order to detect endpoint, particularly at low chloride concentrations.	MOHR, STD. METH.
Lab. 2	No comments.	MOHR
Lab. 3	Time and manipulation good, but endpoint is difficult to see. We do not adjust the pH for our routine work unless sample is definitely known to be acidic or basic.	MOHR
Lab. 4	No comments.	MOHR
Lab. 5	No comments.	MOHR
Lab. 6	No comments.	MOHR, STD. METH.
Lab. 7	This is an old accepted procedure.	MOHR, STD. METH. 10th ED.
Lab. 8	This method is simple and accurate.	MERCURIC NITRATE
Lab. 9	Determined as recommended by Standard Methods using silver nitrate. 1 ml. equals 0.5 mg of chloride.	STD. METH.
Lab. 10	No comments.	MOHR, STD. METH. 10th ED.
Lab. 11	Difficulty in perceiving the endpoint has been met by using a blank for comparison and through the use of the same analysts for this determination. Good precision is always evident; reliable accuracy has been demonstrated on controls in the past.	MOHR, STD. METH. 10th ED.
Lab. 12	Method is good. It is necessary to adjust pH of solution to pH 3.1 before titration with mercuric ion. Important to have this pH the same as that at which titrating solution was standardized.	MERCURIC NITRATE, STD. METH.
Lab. 13	Endpoint not satisfactory.	MOHR
Lab. 14	Endpoint not sharp with 0.01N $AgNO_3$, when chlorides are high.	MOHR
Lab. 15	Chlorides are determined electrometrically in our laboratory using silver nitrate as the titrant.	ELECTROMETRIC
Lab. 16	Convenient and accurate, when the titration is conducted in porcelain dishes.	MOHR, STD. METH.

COMMENTS ON CHLORIDE METHOD

Lab. 17	Samples titrated under a yellow light to the first pinkish-yellow color change which is the same endpoint used to standardize the silver nitrate solution used as the titrant.	MOHR
Lab. 18	Easy to "overshoot" the endpoint.	MOHR
Lab. 19	An excellent method with respect to manipulation, speed, and accuracy. The method is straightforward and simple.	MOHR
Lab. 20	Method satisfactory.	MOHR
Lab. 21	No comments.	MOHR
Lab. 22	No comments.	MOHR
Lab. 23	Very sharp endpoint.	MERCURIC NITRATE, STD. METH. 10th ED.
Lab. 24	We are quite satisfied with the mercuric nitrate titration.	MERCURIC NITRATE, STD. METH. 10th ED.
Lab. 25	No comments.	MOHR
Lab. 26	No difficulties were encountered in titrating chloride in the USPHS sample. This method is considered to be satisfactory with respect to precision and accuracy by this laboratory. Large amounts of natural color tend to mask the endpoint, consequently, giving some difficulty in the titration of this type of water.	MOHR
Lab. 27	Method is simple and easy but endpoint not exact. Difficulty experienced with colored industrial waste samples. The sample was also run by mercuric nitrate method and a value of 215 mg/l obtained but this is not our routine method.	MOHR AND MERCURIC NITRATE
Lab. 28	No comments.	MOHR
Lab. 29	No pH adjustment, 100 ml sample. Yellow light used for titration.	MOHR, STD. METH. 10th ED.
Lab. 30	No comments.	MOHR, STD. METH. 10th ED.
Lab. 31	No comments.	MOHR

ALKALINITY

Of the 31 laboratories performing the alkalinity measurement, 8 groups used two or more methods in reporting results. The prodecures used vary only in the choice of indicator or pH for determining the end point of the titration. The indicators include methyl orange, methyl purple, brom cresol green, brom thymol blue, and "mixed indicator" of brom cresol green and methyl red. The pH chosen for end points ranged from 5.1 to 3.9.

Methyl orange predominates as the choice of colored indicator, but is apparently not satisfactory on the basis of results submitted. The arithmetic mean for 12 methyl orange figures was 21 mg/l with a standard deviation of 5.9 mg/l. Other indicators were not used frequently enough to furnish statistical evidence of success or failure. The most obvious reason for failure of the methyl orange is the subjective human error caused by inability of the individual analysts to detect subtle color changes.

Eighteen groups reported the alkalinity based on electrometric end points but these also varied too widely to furnish valid statistical information. Taken as a group, the 18 laboratories had an arithmetic mean of 18.8 mg/l and a standard deviation of 3.2 mg/l. Substitution of an objective physical end point for a subjective colored end point undoubtedly reduces the potential error.

SUMMARY:

Amount Added	17 mg/l (as $CaCO_3$)
Average Deviation from Amount Added	3.1 mg/l
Standard Deviation	3.4 mg/l
50% Range	2.0 mg/l
Method Most Commonly Used	Electrometric
Method Preferred	Electrometric
Total Number of Observations	41

ALKALINITY AS $CaCO_3$

Amount Added = 17 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	18 18 19	18	1.83	7.82	Electrometric Std. Methods, 10th Edition
1	22 25 22	23	5.78	35.29	Colorimetric Std. Methods
2	19 -- --	19	---	11.76	Methyl Purple
3	19 19 20	19	1.74	13.70	Methyl Purple
3A	17 17 17	17	0.00	0.00	Electrometric
4	16 16 --	16	0.00	5.88	Electrometric
5	17 -- --	17	---	0.00	Electrometric
5A	18 -- --	18	---	5.88	Mixed Indicator
5B	23 -- --	23	---	35.29	Methyl Orange
6	20 19 19	19	1.74	13.70	Electrometric
7	24 24 24	24	0.00	41.20	Methyl Orange

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
8	19 19 --	19	0.00	11.77	Electrometric
8A	21 21 --	21	0.00	23.54	Methyl Orange
9	20 20 20	20	0.00	17.65	Electrometric
10	18 20 19	19	3.53	11.77	Methyl Orange Std. Methods, 10th Edition
11	24 25 25	25	1.32	45.10	Electrometric
12	17 18 16	16	6.25	3.94	Electrometric Std. Methods
13	20 19 21	20	3.35	17.65	Methyl Purple
14	16 16 --	16	0.00	5.89	Electrometric
15	15 16 --	16	3.12	8.83	Electrometric
15A	17 -- --	17	---	0.00	Methyl Orange
16	21 21 --	21	0.00	23.52	Std. Methods
17	20 20 20	20	0.00	17.65	Mixed Indicator
17A	18 18 18	18	0.00	5.89	Electrometric

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
17B	18 18 18	18	0.00	5.89	Methyl Orange
18	18 19 19	19	1.73	9.83	Methyl Purple
18A	18 -- --	18	---	5.89	Electrometric
19	24 -- --	24	---	41.20	Electrometric
19A	19 -- --	19	---	11.78	Brom Cresol Green
20	17 16 --	16	3.12	2.94	Methyl Orange Std. Methods, 10th Edition
21	22 22 22	22	0.00	29.40	Electrometric
22	20 19 --	20	2.50	14.70	Electrometric
23	18 18 18	18	0.00	5.88	Methyl Orange
24	25 25 25	25	0.00	47.00	Electrometric
24A	18 -- --	18	---	5.88	Electrometric
25	18 -- --	18	---	5.89	Methyl Orange

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
26	18 19 19	19	1.74	9.83	Electrometric
27	20 21 21 22	21	2.38	23.52	Electrometric
28	20 20 20	20	0.00	17.65	Electrometric
29	31 29 30	30	2.23	76.50	Methyl Orange Std. Methods, 10th Edition
30	29 -- --	29	---	70.60	Mixed Indicator Std. Methods, 10th Edition
31	18 18 --	18	0.00	5.89	Electrometric

Avg. of the means 19.9
Mean % deviation within labs 1.37
Mean % deviation from amt. added..... 17.95

COMMENTS ON TOTAL ALKALINITY METHOD

Lab. 1 Method satisfactory if interfering color and turbidity can be removed. Endpoint requires experience.

COLORIMETRIC, STD. METH.

Lab. 2 A value of 26 ppm was obtained by the use of methyl orange.

METHYL PURPLE

Lab. 3 Methyl purple gives very good results and is rapid for routine work. Electrometric method is more accurate for precise work, but would be somewhat time consuming for routine work.

ELECTROMETRIC, METHYL PURPLE

Lab. 4 When alkalinity was determined using a mixed indicator of bromcresol green and methyl red and titration carried to the first change (from blue to gray) the values were 17.0, 17.0, average, 17.0 mg/l.

ELECTROMETRIC pH 5.1

Lab. 5 For routine work the plethora of conditions imposed by Standard Methods is impractical. The use of many different endpoints with one indicator is unsound. One indicator equivalence point should be selected or a pH meter should be used and desired deviations checked electrometrically.

ELECTROMETRIC, MIXED IND., METHYL ORANGE

Lab. 6 No comments. ELECTROMETRIC, pH 4.8

Lab. 7 Another established procedure using an acid and methyl orange endpoint.

METHYL ORANGE

Lab. 8 Simple and accurate. METHYL ORANGE

Lab. 9 Sulfuric acid was standardized against a solution prepared by dissolving 1.0599 grams of anhydrous sodium carbonate in one liter of freshly boiled and cooled distilled water. Methyl orange was used as the indicator. Each time as the methyl orange made the slightest change in color, the pH of the mixture was 4.4. Both methyl orange and the pH meter were used for each determination.

METHYL ORANGE & ELECTROMETRIC pH 4.4

Lab. 10 No comments. METHYL ORANGE, STD. METH. 10th ED.

Lab. 11 This determination is conducted routinely electrometrically, the endpoint being read at a pH of 4.0. The result on this reference sample was determined to be 17 mg/liter for an endpoint read at a pH of 5.1 (see 1.1 of General Discussion on Page 35 of "Standard Methods"); using the mixed indicator, a value of 18 mg/liter was obtained.

ELECTROMETRIC, pH 4.0

COMMENTS ON TOTAL ALKALINITY METHOD

Lab. 12 pH meter used routinely in this determination. Endpoint pH chosen as function of alkalinity concentration. In this sample, endpoint chosen was pH 5.1.

ELECTROMETRIC pH 5.1, STD. METH.

Lab. 13 No comments. METHYL PURPLE

Lab. 14 No particular difficulty. The procedure is tedious and time consuming when a pH meter such as Leeds & Northrup 7663-A1 (the only one available in this laboratory) is used; procedure is not used routinely in this lab. No data available on precision or accuracy, except that the curves for duplicate aliquots of Analytical Reference Sample 1-A were superimposable.

The alkalinity as reported is based upon an arbitrary titration endpoint of pH 5.1, as suggested in "Standard Methods", X edition. Titrations to methyl orange endpoint gave duplicate results of 20 and 21 ppm. $CaCO_3$; the endpoints were not sharp, although for most surface waters analyzed by this laboratory, methyl orange endpoints are sharp. Finally, duplicate titrations to the bromthymol blue endpoint at the boiling point gave 17.7 and 17.8 ppm. $CaCO_3$; this procedure is tedious, but gives a sharp endpoint.

ELECTROMETRIC, pH 5.1

Lab. 15 By using an equivalence point of 5.1, the electrometric titrations gave a slightly lower result than the M.O. endpoint, which was also recorded.

ELECTROMETRIC, pH 5.1

Lab. 16 Accurate and convenient. STD. METH.

Lab. 17 The methyl orange endpoint is determined as being the first color change observed and is the same endpoint used in standardizing the titrant. The brom cresol green-methyl red indicator was the mixed indicator used for alkalinity determinations.

ELECTROMETRIC, MIXED IND., METHYL ORANGE

Lab. 18 We find that methyl purple gives us a more precise endpoint than does methyl orange

METHYL PURPLE, ELECTROMETRIC, pH 4.8

Lab. 19 Electrometric endpoint method. The results achieved with this method may be slightly high since we titrate with a standard acid to a pH of 3.92 - the pH which we believe represents the true endpoint of the total alkalinity titration. The method is rapid, easy, and the precision and accuracy is good. Brom Cresol Green Method. This method is not usually employed in our laboratory, but it appears to work very well. The endpoint is easily determined, but the pH of the endpoint would seem to indicate that results might possibly be on the low side. The method is rapid, simple, but the accuracy may be questionable.

ELECTROMETRIC, pH 3.92, BROM CRESOL GREEN

COMMENTS ON TOTAL ALKALINITY METHOD

Lab. 20 — Electrometric titrations are not made routinely on potable waters.

METHYL ORANGE, STD. METH. 10th ED.

Lab. 21 — For a long time we have used the Beckman pH meter model H-2, titrating to pH 4.0, which is the pink of the methyl orange endpoint.

ELECTROMETRIC, pH 4.0

Lab. 22 — No comments. ELECTROMETRIC

Lab. 23 — Would have preferred checking our results with the use of a pH meter but ours is not working at present time. Endpoint of methyl orange is not too distinct.

METHYL ORANGE

Lab. 24 — See attached reprint. ELECTROMETRIC

Lab. 25 — No comments. METHYL ORANGE

Lab. 26 — The total alkalinity was determined by titration with a standard sulfuric acid solution utilizing Beckman Model H2 pH meter to determine the endpoint of the titration (pH 4.5). There were no difficulties encountered in analyzing the USPHS sample. The use of the pH meter to determine the endpoint is far superior to the method which uses visual determination of the endpoint by use of indicators. Precision and accuracy cannot be expected to be better than about 2%.

ELECTROMETRIC, pH 4.5

Lab. 27 — The electrometric method is both simple and accurate with the added advantage that highly colored samples cause no trouble. However, great care must be taken with the meter to make sure readings are correct. The Type I sample was also run using methyl purple as an indicator and a total alkalinity of 18 mg/l was found.

ELECTROMETRIC, pH 4.3

Lab. 28 — No comments. ELECTROMETRIC

Lab. 29 — Methyl orange indicator. Mixed indicator does not appear to be as sharp as methyl orange.

METHYL ORANGE, STD. METH. 10th ED.

Lab. 30 — No comments. MIXED IND., STD. METH. 10th ED.

Lab. 31 — Titrated to pH 4.5. Colored indicator endpoint not run.

ELECTROMETRIC, pH 4.5

NITRITE - 0.20 mg/l

Examination of this group of data with reference to amount reported vs. age of sample indicates that the nitrite nitrogen of the sample was stable. However, only four of the twenty-nine reporting groups found nitrite nitrogen in excess of the amount added. In the absence of any known interferences and with pronounced non-random distribution on the low side, an error in sample preparation must be considered. Since this error (if such an error did occur) is incalculable, the statistical values obtained from this data may be of dubious value.

SUMMARY:

Amount Added	0.20 mg/l
Average Deviation from Amount Added	0.065 mg/l
Standard Deviation	0.041
50% Range	0.04
Method Most Commonly Used	Diazotization
Method Preferred	Same
Total Number of Observations	29

NITRITE NITROGEN

Amount Added = 0.20 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	0.18 0.20 0.18	0.19	5.26	6.50	Diazotization Std. Methods 10th Edition
1	0.26 0.26 0.26	0.26	0.00	30.00	Diazotization Std. Methods
2	0.15 --- ---	0.15	0.00	25.00	Diazotization
3	0.43 0.43 0.43	0.43	0.00	115.00	Diazotization
4	0.17 0.17 0.17	0.17	0.00	15.00	Diazotization
5	0.15 0.17 ---	0.16	6.25	20.00	Diazotization
6	0.20 0.20 0.20	0.20	0.00	0.00	Diazotization
7	0.22 0.22 0.22	0.22	0.00	10.00	Diazotization Std. Methods, 10th Edition
8	0.18 0.18 ---	0.18	0.00	10.00	Diazotization
9	--- --- ---	---	---	---	----------
10	0.20 0.20 0.18	0.19	5.26	5.00	Diazotization Std. Methods, 10th Edition

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	0.18 0.18 0.18	0.18	0.00	10.00	Diazotization
12	0.16 0.16 0.17	0.16	0.00	20.00	Diazotization Std. Methods
13	0.17 0.17 0.17	0.17	0.00	15.00	Diazotization Std. Methods, 10th Edition
14	0.16 0.16 ---	0.16	0.00	20.00	Diazotization Std. Methods, 10th Edition
15	0.15 0.15 ---	0.15	0.00	25.00	Diazotization
16	--- --- ---	---	---	---	----------
17	0.16 0.17 0.17	0.17	0.00	15.00	Diazotization
18	0.15 0.15 0.15	0.15	0.00	25.00	Diazotization
19	0.16 0.17 0.18	0.17	3.94	15.00	Diazotization
20	0.15 0.15 ---	0.15	0.00	25.00	Diazotization
21	0.14 0.14 0.15	0.14	2.36	30.00	Diazotization
22	0.16 0.17 ---	0.16	3.12	20.00	Diazotization

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
23	--- --- ---	---	---	---	----------
24	0.14 --- ---	0.14	---	30.00	Diazotization Std. Methods, 10th Edition
24A	0.14 --- ---	0.14	---	30.00	Diazotization Std. Methods, 10th Edition
25	0.20 --- ---	0.20	---	0.00	Diazotization Std. Methods, 9th Edition
26	0.30 0.30 ---	0.30	0.00	50.00	Diazotization
27	0.13 0.13 ---	0.13	0.00	35.00	Diazotization Std. Methods, 9th Edition
28	0.16 0.16 0.16	0.16	0.00	20.00	Diazotization
29	0.16 0.15 0.16	0.16	2.06	21.61	Diazotization Std. Methods, 10th Edition
30	0.49 --- ---	0.49	---	145.00	Diazotization Std. Methods, 9th Edition
31	0.16 0.17 0.17	0.17	2.06	15.00	Hellige

Avg. of the means 0.19
Mean % deviation within labs 1.17
Mean % deviation from amt. added 26.79

COMMENTS ON NITRITE NITROGEN METHOD

Lab. 1	Method is satisfactory.	DIAZOTIZATION, STD. METH.
Lab. 2	No comments.	DIAZOTIZATION
Lab. 3	Very sensitive and rapid. Done only on industrial wastes and sewage.	DIAZOTIZATION
Lab. 4	The colored solution developed in the nitrite test is apparently stable for at least 18 hours provided that the concentration is not higher than .004 mg. NO_2/N in 50 ml. Higher concentrations form precipitates on standing which settle out.	DIAZOTIZATION
Lab. 5	No difficulty encountered here.	DIAZOTIZATION
Lab. 6	No comments.	DIAZOTIZATION
Lab. 7	This method works very well, however it is very sensitive, requiring large dilutions if much NO_2 is present. We could only use 2 ml of the water supplied for color development.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 8	A simple method, duplicates checking well. Not a routine analysis.	DIAZOTIZATION
Lab. 9	We do not run the NO_2/N as samples arrive usually from several days up to two or three weeks after collection.	
Lab. 10	No comments.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 11	This method is considered to be sufficiently simple and rapid and good precision and accuracy have been obtained.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 12	No comments. Method is good.	DIAZOTIZATION, STD. METH.
Lab. 13	No comments.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 14	High blank values have been chief difficulty, due to nitrite in distilled water. Difficulty overcome by treating distilled water with H_2SO_4 and $KMnO_4$ and redistilling. The method is classical.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 15	The final reading was made on a spectrophotometer with a wavelength of 520.	DIAZOTIZATION
Lab. 16	Not run.	

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
23	--- --- ---	---	---	---	---
24	0.14 --- ---	0.14	---	30.00	Diazotization Std. Methods, 10th Edition
24A	0.14 --- ---	0.14	---	30.00	Diazotization Std. Methods, 10th Edition
25	0.20 --- ---	0.20	---	0.00	Diazotization Std. Methods, 9th Edition
26	0.30 0.30 ---	0.30	0.00	50.00	Diazotization
27	0.13 0.13 ---	0.13	0.00	35.00	Diazotization Std. Methods, 9th Edition
28	0.16 0.16 0.16	0.16	0.00	20.00	Diazotization
29	0.16 0.15 0.16	0.16	2.06	21.61	Diazotization Std. Methods, 10th Edition
30	0.49 --- ---	0.49	---	145.00	Diazotization Std. Methods, 9th Edition
31	0.16 0.17 0.17	0.17	2.06	15.00	Hellige

Avg. of the means 0.19
Mean % deviation within labs 1.17
Mean % deviation from amt. added 26.79

COMMENTS ON NITRITE NITROGEN METHOD

Lab. 1	Method is satisfactory.	DIAZOTIZATION, STD. METH.
Lab. 2	No comments.	DIAZOTIZATION
Lab. 3	Very sensitive and rapid. Done only on industrial wastes and sewage.	DIAZOTIZATION
Lab. 4	The colored solution developed in the nitrite test is apparently stable for at least 18 hours provided that the concentration is not higher than .004 mg. NO_2/N in 50 ml. Higher concentrations form precipitates on standing which settle out.	DIAZOTIZATION
Lab. 5	No difficulty encountered here.	DIAZOTIZATION
Lab. 6	No comments.	DIAZOTIZATION
Lab. 7	This method works very well, however it is very sensitive, requiring large dilutions if much NO_2 is present. We could only use 2 ml of the water supplied for color development.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 8	A simple method, duplicates checking well. Not a routine analysis.	DIAZOTIZATION
Lab. 9	We do not run the NO_2/N as samples arrive usually from several days up to two or three weeks after collection.	
Lab. 10	No comments.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 11	This method is considered to be sufficiently simple and rapid and good precision and accuracy have been obtained.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 12	No comments. Method is good.	DIAZOTIZATION, STD. METH.
Lab. 13	No comments.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 14	High blank values have been chief difficulty, due to nitrite in distilled water. Difficulty overcome by treating distilled water with H_2SO_4 and $KMnO_4$ and redistilling. The method is classical.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 15	The final reading was made on a spectrophotometer with a wavelength of 520.	DIAZOTIZATION
Lab. 16	Not run.	

COMMENTS ON NITRITE NITROGEN METHOD

Lab. 17	No comments.	DIAZOTIZATION
Lab. 18	Fast and very sensitive.	DIAZOTIZATION
Lab. 19	Dimethyl-alpha-naphthylamine method. The color produced with dimethyl-alpha-naphthylamine is superior in stability, intensity and brilliance to that with alpha-naphthylamine. The method boasts ease of manipulation, rapidity and excellent accuracy.	DIAZOTIZATION, MODIFIED
Lab. 20	Glassware was acid rinsed before use. Comparison made colorimetrically with permanent standards.	DIAZOTIZATION
Lab. 21	No comments.	DIAZOTIZATION
Lab. 22	No comments.	DIAZOTIZATION
Lab. 23	Not routinely done in this lab.	
Lab. 24	No comments.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 25	No comments.	DIAZOTIZATION, STD. METH. 9th ED. HELLIGE
Lab. 26	No difficulties were encountered. A procedure of this laboratory is to repurify a small quantity of the alpha-naphthylamine prior to the time of analysis. This eliminates erratic results due to decomposition and a varied manufacturers composition of the reagent. The purified reagent is best stored in a refrigerated dessicator.	DIAZOTIZATION
Lab. 27	No comments.	DIAZOTIZATION, STD. METH. 9th ED.
Lab. 28	No comments.	DIAZOTIZATION
Lab. 29	10 ml sample - 0.2 ml of reagents. No pH adjustment, five minute waiting period after sulfanilic acid addition, ten minute waiting period before reading. Coleman Model 6A spectrophotometer.	DIAZOTIZATION, STD. METH. 10th ED.
Lab. 30	No comments.	DIAZOTIZATION, STD. METH. 9th ED.
Lab. 31	No comments.	HELLIGE

NITRATE - 1.3 mg/l

Of the 33 reported values for nitrate nitrogen, 27 were obtained using the phenoldisulfonic acid method. As in the preceding Type I sample, the results are almost uniformly low. It is believed that the nitrate ion in this sample is stable and indeed, the results reported do not indicate any progressive diminution with regard to aging. Measurements in the ARS laboratory spanning a period of more than 60 days did not show any decrease in the nitrate concentration.

Eleven laboratories reported using ammonium hydroxide for neutralization of the phenoldisulfonic acid but these results as a unit are not superior to the remainder of the group. It can only be concluded that with, or without correction for chloride interference, the phenoldisulfonic acid method does not give reliable results for most operators. Actually, the figures given below for average deviation and standard deviation would probably be much larger on a sewage type sample.

The other methods used, reduction or brucine, were not used by enough groups to be statistically significant. However, the brucine procedure, used by one ARS member and by one special participant, (not included in the report) did obtain excellent results.

SUMMARY:

Amount Added	1.3 mg/l
Average Deviation from Amount Added	0.35 mg/l
Standard Deviation	0.41
50% Range	0.4 mg/l
Method Most Commonly Used	phenoldisulfonic acid
Method Preferred	No choice
Total Number of Observations	33

NITRATE NITROGEN

Amount Added = 1.3 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	1.1 1.0 1.1	1.1	3.33	17.70	PDA Std. Methods, 10th Edition
1	0.9 0.9 1.0	0.9	3.33	28.30	PDA Std. Methods
2	1.6 --- ---	1.6	0.00	23.08	PDA
3	1.6 1.6 1.6	1.6	0.00	23.08	PDA Std. Methods, 10th Edition
4	1.0 1.0 ---	1.0	0.00	23.08	PDA
5	0.9 0.9 ---	0.9	0.00	30.77	PDA Std. Methods, 10th Edition
6	0.8 0.8 0.8	0.8	0.00	38.45	PDA Std. Methods
7	0.9 0.9 0.9	0.9	0.00	30.77	PDA Std. Methods 10th Edition
8	1.0 1.0 ---	1.0	0.00	23.08	PDA
9	0.9 0.9 0.9	0.9	0.00	30.77	PDA
10	1.4 1.4 1.4	1.4	0.00	7.70	PDA Std. Methods, 10th Edition

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	1.4 1.4 1.4	1.4	0.00	7.70	PDA Std. Methods, 10th Edition
12	1.0 1.0 1.0	1.0	5.00	23.08	PDA Std. Methods
13	0.9 1.1 1.0	1.0	7.00	23.08	PDA Std. Methods 10th Edition
14	1.2 1.3 ---	1.2	4.16	3.85	Reduction
15	0.8 0.8 ---	0.8	0.00	38.40	PDA
16	1.2 1.2 ---	1.2	0.00	7.70	PDA Std. Methods
17	0.7 0.7 0.7	0.7	0.00	46.20	PDA
17A	0.7 0.7 0.8	0.7	4.29	43.90	Reduction
18	1.1 1.1 1.1	1.1	0.00	15.40	PDA
19	0.6 0.6 ---	0.6	0.00	54.00	PDA
20	1.2 1.0 ---	1.1	9.10	15.40	PDA Std. Methods, 10th Edition
21	1.0 1.0 1.0	1.0	0.00	23.07	PDA

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
22	0.6 0.5 ---	0.6	8.30	57.7	PDA
23	1.4 1.4 1.1	1.3	10.24	12.69	PDA Std. Methods, 10th Edition
24	1.2 --- ---	1.2	---	7.70	Brucine
24A	1.2 --- ---	1.2	---	7.70	Brucine
25	0.8 --- ---	0.8	---	38.42	Reduction
26	0.8 0.8 ---	0.8	0.00	38.42	PDA
27	2.0 2.0 ---	2.0	0.00	53.90	PDA Std. Methods, 10th Edition
28	0.4 0.5 0.5	0.5	6.60	64.10	PDA
29	0.9 0.9 0.9	0.9	0.00	30.80	PDA Std. Methods, 10th Edition
30	1.6 --- ---	1.6	---	23.10	PDA Std. Methods, 9th Edition
31	1.2 1.2 1.2	1.2	0.00	7.70	PDA

Avg. of the means 1.06
Mean % deviation within labs 2.04
Mean % deviation from amt. added..... 27.81

COMMENTS ON NITRATE NITROGEN METHOD

Lab. 1 — Method is very satisfactory. Incomplete precipitation of silver may be a problem but we do not ordinarily encounter high chloride concentrations (state-wide average for ground waters is 10 ppm).
PDA, STD. METH.

Lab. 2 — Determinations made without removal of chloride were about one half of the amount shown.
PDA

Lab. 3 — We use concentrated ammonium hydroxide and read on a Spectronic "20" at 410 mμ.
PDA, STD. METH. 10th ED.

Lab. 4 — Nitrate nitrogen was also determined with the polarograph. Results were as follows: 1.4, 1.26, 1.35, average, 1.3 mg/l. Our normal phenoldisulfonic acid procedure does not call for chloride removal. Under these conditions, we would have reported 1.3 mg/l.
PDA

Lab. 5 — In our opinion, chlorides do not significantly interfere when NaOH is used. NH_4OH with silver produces an off shade that is difficult to compare.
PDA, STD. METH.

Lab. 6 — No comments.
PDA, STD. METH.

Lab. 7 — We have always used ammonium hydroxide for color formation.
PDA, STD. METH. 10th ED.

Lab. 8 — Simple and accurate.
PDA

Lab. 9 — Most of the chlorides are removed by treating with silver sulfate solution. Ammonium hydroxide was used for both the standards and the samples, for neutralizing the acid.
PDA

Lab. 10 — No comments.
PDA, STD. METH. 10th ED.

Lab. 11 — The use of potassium or ammonium hydroxide yields essentially the same results. Potassium hydroxide is preferred in that there is accordingly less chance of ammonia contamination of the laboratories. Determinations which did not include treatment to remove chloride interference resulted in values of 0.8 mg/l (KOH) and 0.9 mg/l (NH_4OH).
PDA, STD. METH. 10th ED.

Lab. 12 — Method O.K. Concentrated NH_4OH used for neutralization of phenoldisulfonic acid reagent. Chlorides removed with Ag_2SO_4.
PDA, STD. METH.

Lab. 13 — No comments.
PDA, STD. METH. 10th ED.

COMMENTS ON NITRATE NITROGEN METHOD

Lab. 14 — No unusual difficulties have been encountered, but time consuming; NH_3 must first be removed, and reduction takes place overnight. Insufficient data on precision and accuracy. Method used in preference to phenoldisulfonic acid method because nitrate determinations are made infrequently, and preparation of special reagent for latter method not warranted. For higher nitrate concentrations, the m-xylenol method is used in this laboratory, although the manipulations are awkward.

REDUCTION

Lab. 15 — Silver sulfate was used for chloride elimination and ammonium hydroxide for final neutralization.

PDA

Lab. 16 — Method is good and accurate, although time consuming.

PDA, STD. METH.

Lab. 17 — No comments.

PDA AND REDUCTION

Lab. 18 — Neutralization with NH_4OH gives a better standard curve and less trouble with hydroxides than does KOH.

PDA

Lab. 19 — Somewhat time consuming. In cases where the chloride ion must be precipitated with silver sulfate, there may possibly be some interference due to the presence of silver ion. If potassium hydroxide is used instead of ammonium hydroxide, a brownish precipitate invariably appears which must be filtered off - sometimes yielding an off-color solution. The use of ammonium hydroxide, however, apparently solves this particular difficulty. The accuracy of the method is somewhat limited because of the difficulties involved in overcoming the chloride interference.

PDA

Lab. 20 — Concentrated NH_4OH cannot be used for neutralization because ammonia determinations are made in the same room.

PDA, STD. METH. 10th ED.

Lab. 21 — We used NH_4OH for neutralization but prefer NaOH solution in a water laboratory in order to prevent contamination of our ammonium nitrogen stills.

PDA

Lab. 22 — No comments.

PDA

Lab. 23 — Concentrated ammonium hydroxide used. Obtained same results from removal of chlorides with silver sulfate as we did from taking a small sample containing less than 2 mg of chloride.

PDA, STD. METH. 10th ED.

Lab. 24 — See attached manuscript.

BRUCINE

COMMENTS ON NITRATE NITROGEN METHOD

Lab. 25	No comments.	REDUCTION
Lab. 26	The colorimetric phenoldisulfonic acid method utilizing the neutralization of the acid with a concentrated ammonium hydroxide solution was used in the determination of nitrate nitrogen. The optical density of the sample was determined by a Bausch and Lomb "Spectronic 20" spectrophotometer. No difficulties were encountered in this determination. The interfering chloride ion was precipitated with silver sulfate. This is a good method for determining nitrate concentrations below about 10 ppm. Precision and accuracy would be considered fairly good below this value. Increasing error is encountered for higher concentrations.	PDA
Lab. 27	No comments.	PDA. STD. METH. 10th ED.
Lab. 28	No comments.	PDA
Lab. 29	10 ml sample - 0.5 ml phenoldisulfonic acid 5.5 ml distilled water, 4 ml 6N KOH - Coleman 6A spectrophotometer - 10 mm tubes. Before chloride removed, sample gave average value of 0.6.	PDA. STD. METH. 10th ED.
Lab. 30	No comments.	PDA. STD. METH. 9th ED.
Lab. 31	No comments.	PDA

SODIUM (8 mg/1) and POTASSIUM (3.6 mg/1)

For the sodium and potassium measurements, the flame technique is the only convenient method available. For these two measurements, 24 laboratories submitted sodium analyses and 23 submitted potassium results. All of the determinations (with 2 exceptions) were carried out using flame photometers.

Inspection of the data, sodium vs. potassium would seem to indicate that the sodium measurement is more difficult to perform. In practice, there is undoubtedly a greater chance for sodium contamination of the sample by the operator which accounts for the greater deviations in the sodium data. It appears, however, that both sodium and potassium can be easily measured in normal waters with or without special techniques provided that extraneous sodium and potassium contamination are avoided.

SUMMARY:	Na	K
Amount Added	8 mg/1	3.6 mg/1
Average Deviation from Amount Added	1.7	0.43
95% Standard Deviation	1.3	0.36
50% Range	1.0	0.30
Method Most Commonly Used	Flame	Flame
Method Preferred	Flame	Flame
Total Number of Observations	24	23

SODIUM

Amount Added = 8 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	7.4 7.4 7.5	7.4	0.40	8.11	Flame Std. Methods, 10th Edition
1	--- --- ---	---	---	---	----------
2	9 --- ---	9	---	12.50	Flame - Beckman, DR
3	--- --- ---	---	---	---	----------
4	9 10 9	9	0.33	16.66	Flame - Coleman
5	8 8 ---	8	0.00	0.00	Flame - Beckman, DU
6	9 9 9	9	0.00	12.50	Flame Std. Methods, 10th Edition
7	9 9 9	9	0.00	12.50	Flame - Beckman, DU Std. Methods, 10th Edition
8	10 10 ---	10	0.00	25.00	Flame
9	9 9 9	9	0.00	12.50	Flame - Beckman, DR
10	--- --- ---	---	---	---	----------

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	--- --- ---	---	---	---	----------
12	8 8 10 8	9	11.10	6.25	Flame
13	--- --- ---	---	---	---	----------
14	8 8 ---	8	0.00	0.00	Gravimetric
15	9 8 ---	8	6.25	6.25	Flame
16	--- --- ---	---	---	---	----------
17	--- --- ---	---	---	---	----------
18	8 8 9	8	4.13	4.13	Flame
19	9 --- ---	9	---	12.50	Flame
20	10 10 ---	10	0.00	25.00	Flame Std. Methods, 10th Edition
21	8 9 9	9	3.70	8.37	Flame
22	8 9 ---	9	5.56	6.25	Flame

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
23	13 14 13	13	2.54	66.63	Flame
24	8 --- ---	8	---	0.00	Flame - Baird Std. Methods, 10th Edition
24A	8 --- ---	8	---	0.00	Flame - Baird Std. Methods, 10th Edition
25	--- --- ---	---	---	---	----------
26	6.4* 7.6 8.8	7.6	9.73	9.50	Flame - Perkin-Elmer *10 Replicates submitted
27	6.2 --- ---	6.2	---	22.50	Flame - Perkin-Elmer
28	10 10 10	10	0.00	25.00	Flame - Beckman, DU
29	9 8 9 9	9	2.78	9.38	Flame - Beckman, DU
30	17 --- ---	17	---	112.50	Gravimetric
31	17 18 18	18	1.83	120.75	Flame

Avg. of the means 9.6
Mean % deviation within labs 2.54
Mean % deviation from amt. added..... 21.42

COMMENTS ON SODIUM METHOD

Lab. 1	Not run.	
Lab. 2	No comments.	FLAME, DIRECT READING BECKMAN
Lab. 3	Not run.	
Lab. 4	No comments.	FLAME, COLEMAN
Lab. 5	Used Beckman DU Flame Spectrophotometer with photomultiplier tube, automatic scanner and Brown recorder.	FLAME, BECKMAN DU
Lab. 6	No comments.	FLAME, STD. METH. 10th ED.
Lab. 7	We are using a Beckman DU Spectrophotometer with a flame and photomultiplier attachment and an oxygen acetylene burner. We have attempted to establish operating conditions which will give us acceptable results for routine water analysis where extreme accuracy is not essential.	FLAME, BECKMAN DU WITH PHOTOMULTIPLIER STD. METH. 10th ED.
Lab. 8	Simple and rapid. Not a routine analysis.	FLAME
Lab. 9	This determination was made on a Beckman Direct Reading Flame Photometer. To obtain the milligrams per liter, meq/l were multiplied by the atomic weight of sodium. The instrument was standardized with a mixed solution of sodium and potassium obtained from the company and diluted by taking 5 ml and diluting it to 500 ml as recommended.	FLAME, DIRECT READING BECKMAN
Lab. 10	Not run.	
Lab. 11	Not run.	
Lab. 12	Lithium internal standard used at 500 mg/l concentration.	FLAME
Lab. 13	We determine these two ions by difference. We feel that for our purpose, this is sufficiently accurate and of about the same degree of accuracy as those obtained from the flame method.	
Lab. 14	Chief difficulty is that with waters high in $CaSO_4$, as present sample, crystallization of $CaSO_4$ takes place when sample is evaporated. Evaporation to 1-2 ml. was completed in centrifuge tube, mixture was centrifuged, supernatant separated, and residue washed once with 1 ml distilled water by centrifuging. Supernatant added to first supernatant and determination continued. Method somewhat tedious, but is best available in absence of a flame photometer. Elimination of difficulties due to crystallization of $CaSO_4$ could probably be accomplished by first passing sample through an anion-exchange resin in the chloride form.	GRAVIMETRIC

COMMENTS ON SODIUM METHOD

Lab. 15 No comments. FLAME

Lab. 16 Not run.

Lab. 17 Not run.

Lab. 18 Standard curve of 0-100 used. We have not had any success with buffers. Method has not been investigated enough that we are aware of interferences involved.
FLAME

Lab. 19 Calcium and sulfate are the chief interferences. The sulfate ion is completely removed by passing a portion of the sample through an ion-exchange resin (Rohm & Haas IR-401). The calcium interference is cancelled out by comparing with standards containing comparable amounts of calcium in the sample. This can be easily accomplished since apparently calcium is determined readily without interference from other cations. Method is rapid; accuracy is good.
FLAME

Lab. 20 The most difficult part of the analysis is the standardization of the flame photometer. Probably this is also the greatest source of error.
FLAME, STD. METH. 10th ED.

Lab. 21 No comments. FLAME

Lab. 22 No comments. FLAME

Lab. 23 We do not use internal standards. Have had excellent results with recovery tests on known samples.
FLAME

Lab. 24 A Baird flame photometer is used.
FLAME, BAIRD, STD. METH. 10th ED.

Lab. 25 Not run.

Lab. 26 Sodium was determined using a lithium internal standard. No difficulties were experienced in determining the sodium concentration of the USPHS sample. Sodium can be determined rapidly by use of the flame photometer. Accuracy and precision for low concentrations approach gravimetric procedures. Due to the inherent error involved in diluting concentrated samples, a proportionately larger error is involved in analyzing more concentrated waters.
FLAME, PERKIN-ELMER, 52C

Lab. 27 Sodium was determined using a lithium internal standard. No difficulties were experienced. Accuracy and precision for low concentrations approach gravimetric procedures. Necessity for dilution of high concentrations gives proportionately larger errors.
FLAME, PERKIN-ELMER, 52C

COMMENTS ON SODIUM METHOD

Lab. 28	No comments.	FLAME, BECKMAN DU
Lab. 29	No comments.	FLAME, BECKMAN DU WITH PHOTOMULTIPLIER
Lab. 30	No comments.	GRAVIMETRIC, AOAC, 8th ED.
Lab. 31	Run using sodium buffer as per West, Folse & Montgomery; Anal. Chem. 22, No. 5, 1950.	FLAME

POTASSIUM

Amount Added = 3.6 mg/l

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
SEC	3.8 3.8 3.8	3.8	0.00	5.56	Flame Std. Methods, 10th Edition
1	--- --- ---	---	---	---	----------
2	3.4 --- ---	3.4	---	5.56	Flame - Beckman, DR
3	--- --- ---	---	---	---	----------
4	4.0 4.0 ---	4.0	0.00	11.11	Flame - Coleman
5	3.7 3.7 ---	3.7	0.00	2.78	Flame - Beckman, DU
6	3.2 3.2 3.2	3.2	0.00	11.10	Flame Std. Methods, 10th Edition
7	3.6 3.6 3.6	3.6	0.00	0.00	Flame - Beckman, DU Std. Methods, 10th Edition
8	4.0 4.0 ---	4.0	0.00	11.10	Flame
9	3.6 3.6 3.6	3.6	0.00	0.00	Flame - Beckman, DR
10	--- --- ---	---	---	---	----------

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
11	--- --- ---	---	---	---	----------
12	3.3 3.3 2.6	3.1	9.69	14.72	Flame
13	--- --- ---	---	---	---	----------
14	3.0 2.9 ---	2.9	17.23	18.05	Gravimetric
15	3.8 3.8 ---	3.8	0.00	5.56	Flame
16	--- --- ---	---	---	---	----------
17	--- --- ---	---	---	---	----------
18	4.0 3.8 3.8	3.9	2.53	7.50	Flame
19	3.8 --- ---	3.8	---	5.56	Flame
20	3.0 3.0 ---	3.0	0.00	16.67	Flame Std. Methods, 10th Edition
21	4.4 4.0 3.9	4.1	4.88	13.89	Flame
22	4.0 4.0 ---	4.0	0.00	11.10	Flame

Lab No.	Results	Mean	% Deviation Within Labs	% Deviation From Amt. Added	Method
23	--- --- ---	---	---	---	----------
24	3.6 --- ---	3.6	---	0.00	Flame - Baird Std. Methods, 10th Edition
24A	3.4 --- ---	3.4	---	5.56	Flame - Baird Std. Methods, 10th Edition
25	--- --- ---	---	---	---	----------
26	3.2* 3.2 3.4	3.3	7.28	10.10	Flame - Perkin-Elmer *10 Replicates submitted
27	3.4 --- ---	3.4	---	5.56	Flame - Perkin-Elmer
28	3.6 3.5 3.3	3.4	3.91	3.68	Flame - Beckman, DU
29	4.9 4.7 4.6 4.5	4.7	2.66	29.80	Flame Std. Methods, 10th Edition
30	4.1 --- ---	4.1	---	13.89	Gravimetric
31	3.0 3.0 ---	3.0	0.00	15.55	Flame

Avg. of the means 3.6
Mean % deviation within labs 2.67
Mean % deviation from amt. added..... 9.36

COMMENTS ON POTASSIUM METHOD

Lab. 1	Not run.	
Lab. 2	No comments.	FLAME, DIRECT READING BECKMAN
Lab. 3	Not run.	
Lab. 4	No comments.	FLAME, COLEMAN
Lab. 5	See Sodium Method.	FLAME, BECKMAN DU
Lab. 6	No comments.	FLAME, STD. METH. 10th ED.
Lab. 7	Same comment as for Sodium.	FLAME, BECKMAN DU WITH PHOTOMULTIPLIER STD. METH. 10th ED.
Lab. 8	Simple and rapid. Not a routine analysis. The sodium and potassium tests were performed by one chemist, the remainder by another.	FLAME
Lab. 9	The same instrument was used as was used for sodium and was standardized for potassium on the scale prepared for that purpose. To obtain the milligrams per liter, the milliequivalents/liter were multiplied by the atomic weight of potassium.	FLAME, DIRECT READING BECKMAN
Lab. 10	Not run.	
Lab. 11	Not run.	
Lab. 12	Lithium internal standard used at 500 mg/l concentration.	FLAME
Lab. 13	Not run.	
Lab. 14	Same comments as for Sodium Method. Method is tedious, but seems best available for low concentrations in absence of flame photometer. The procedure used was that given by Ismail & Harwood, Analyst, V.62, p. 443 (1937).	GRAVIMETRIC
Lab. 15	No comments.	FLAME
Lab. 16	Not run.	
Lab. 17	Not run.	
Lab. 18	Same as Sodium Method. Standard curve of 0-3 used.	FLAME

COMMENTS ON POTASSIUM METHOD

Lab. 19	This determination is subject to background interference. This is held to a minimum by comparing with standards containing comparable amounts of calcium and sodium as the sample. Sulfate ion is eliminated by passing portion of sample through anion exchange resin IR 401. Method is rapid; accuracy is fair.	FLAME
Lab. 20	Same as for Sodium.	FLAME, STD. METH. 10th ED.
Lab. 21	No comments.	FLAME
Lab. 22	No comments.	FLAME
Lab. 23	Not run.	
Lab. 24	No comments.	FLAME, BAIRD, STD. METH. 10th ED.
Lab. 25	Not run.	
Lab. 26	All comments that apply to the sodium determination would be applicable to the potassium determination.	FLAME, PERKIN-ELMER, 52C
Lab. 27	Same comments as for Sodium.	FLAME, PERKIN-ELMER, 52C
Lab. 28	No comments.	FLAME, BECKMAN DU
Lab. 29	Same instrument as for Sodium. This is not a routine procedure in this laboratory.	FLAME, STD. METH. 10th ED.
Lab. 30	No comments.	GRAVIMETRIC, AOAC, 8th ED.
Lab. 31	No comments.	FLAME

SUMMARY OF DATA

	Calcium	Magnesium	Hardness	Alkalinity
Amount Added, mg/l	120	75	608	17
Number of Analyses	33	32	34	41
Arithmetic Mean	119	76	614	19.9
Average Deviation	5.4	3.3	13	3.1
Standard Deviation	5.5	2.7	13.7	3.4
Number of Methods Used	6	7	3	4
Method #1	Versene	Versene	Versene	Electrometric
Number of Users	(20)	(9)	(31)	(17)
Standard Deviation	4.2	3.0	13.7	3.2
Method #2	Volumetric Permanganate	Gravimetric	Calculation	Methyl Orange
Number of Users	(5)	(6)	(2)	(10)
Standard Deviation	2.1	1.6	-	5.0

SUMMARY OF DATA

Chloride	Sulfate	Nitrite	Nitrate	Sodium	Potassium
219	288	0.20	1.3	8	3.6
31	38	29	33	24	23
218	283	0.19	1.06	9.6	3.6
4.0	14.1	.065	0.35	1.7	0.43
4.1	10.1	.041	0.41	1.3	0.36
3	4	1	3	2	2
Mohr	Gravimetric	Diazotization	Phenoldisulfonic	Flame	Flame
(23)	(21)	(29)	(27)	(23)	(22)
6.2	9.2	.041	0.41	1.3	0.36
Mercuric Nitrate	Turbidimetric	-	Reduction, Brucine	-	-
(6)	(10)		(3) & (2)		
4.5	32	-	-	-	-

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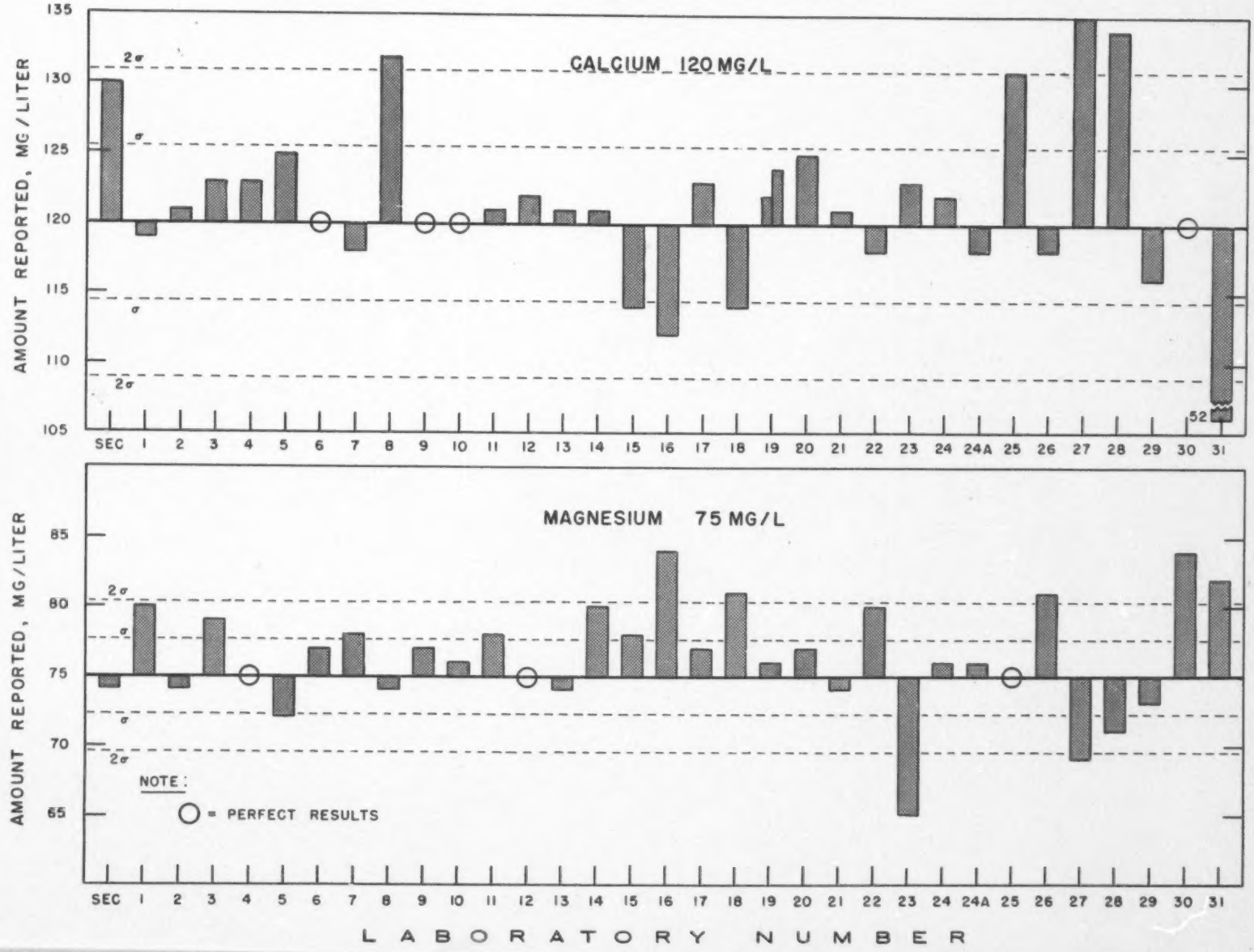

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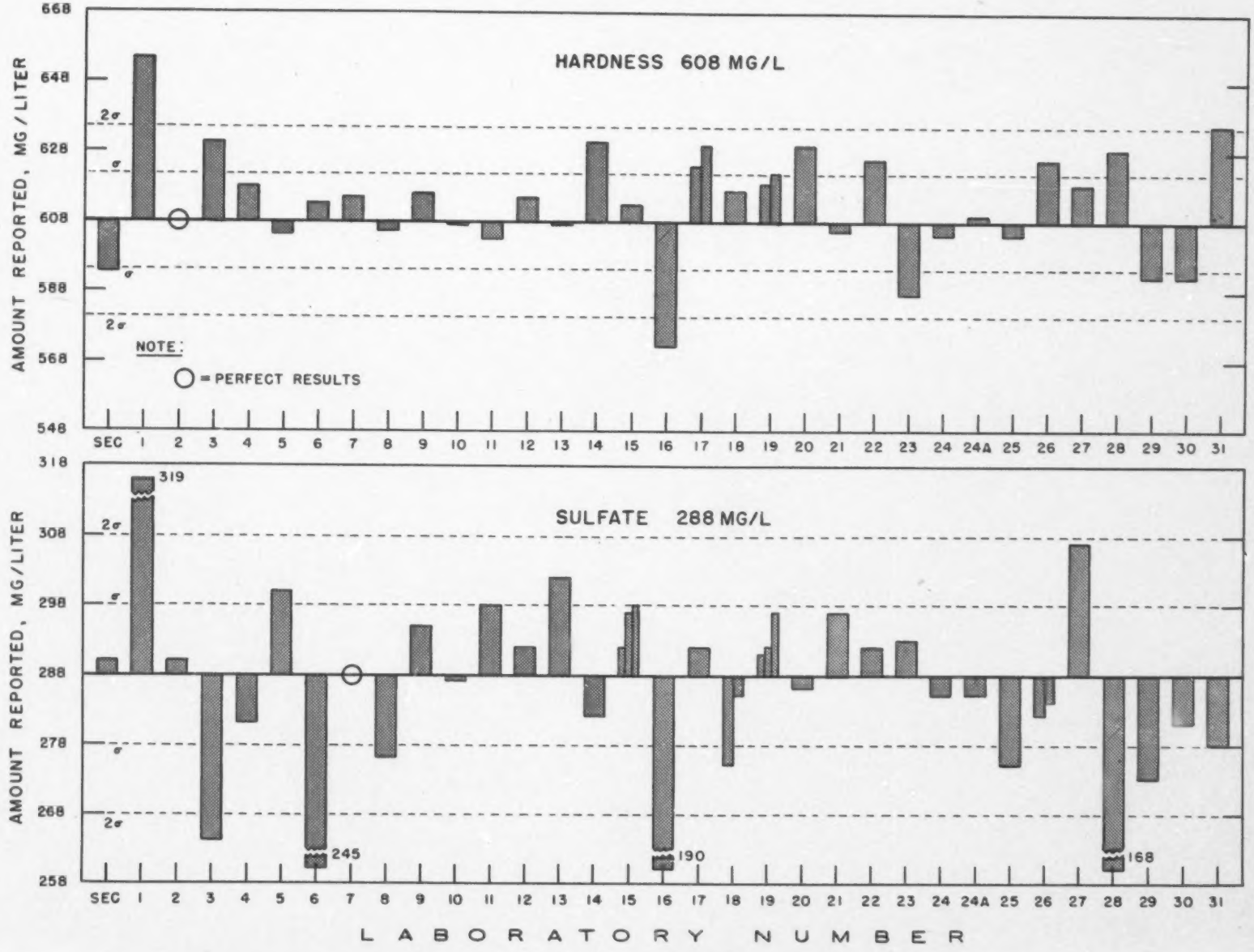
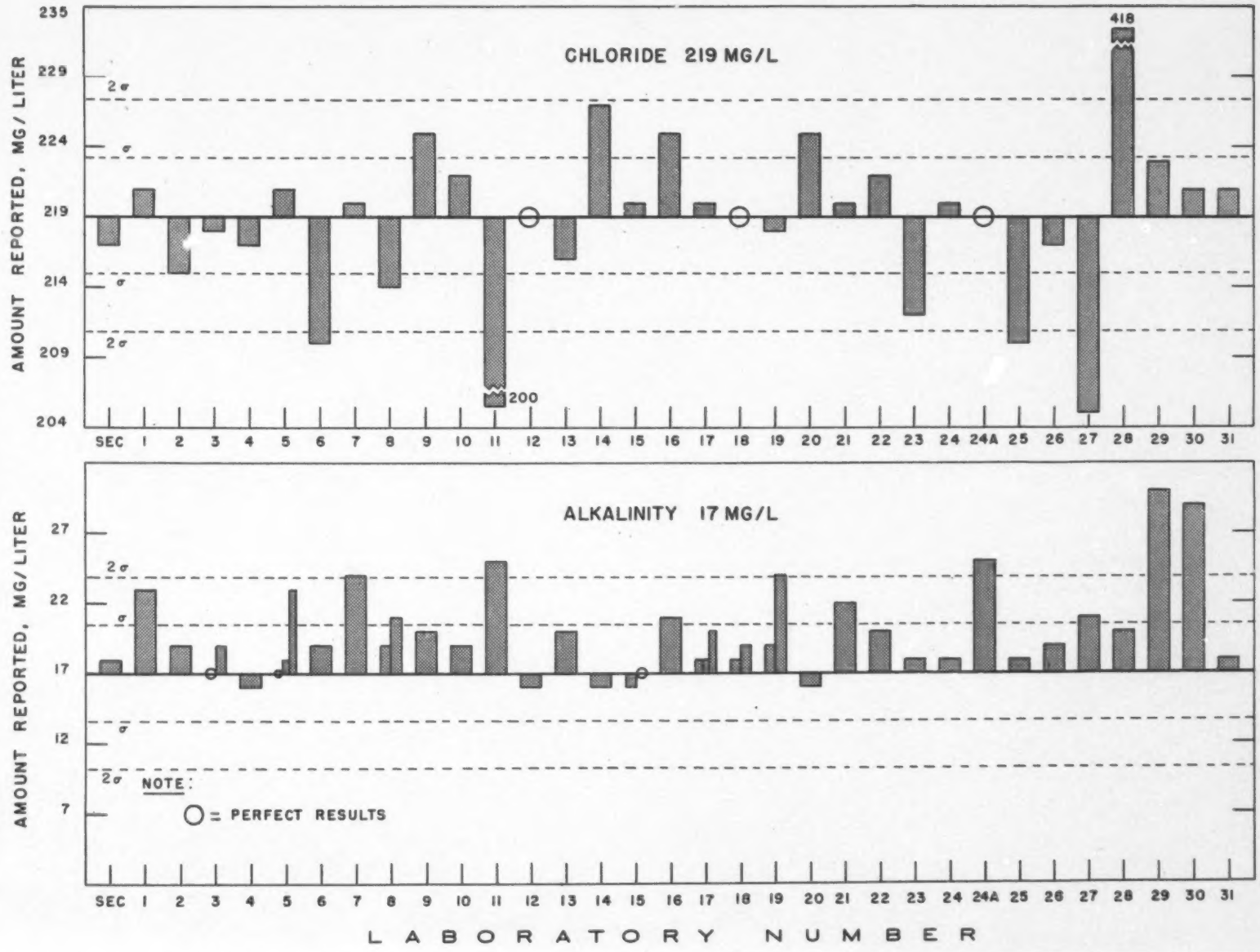
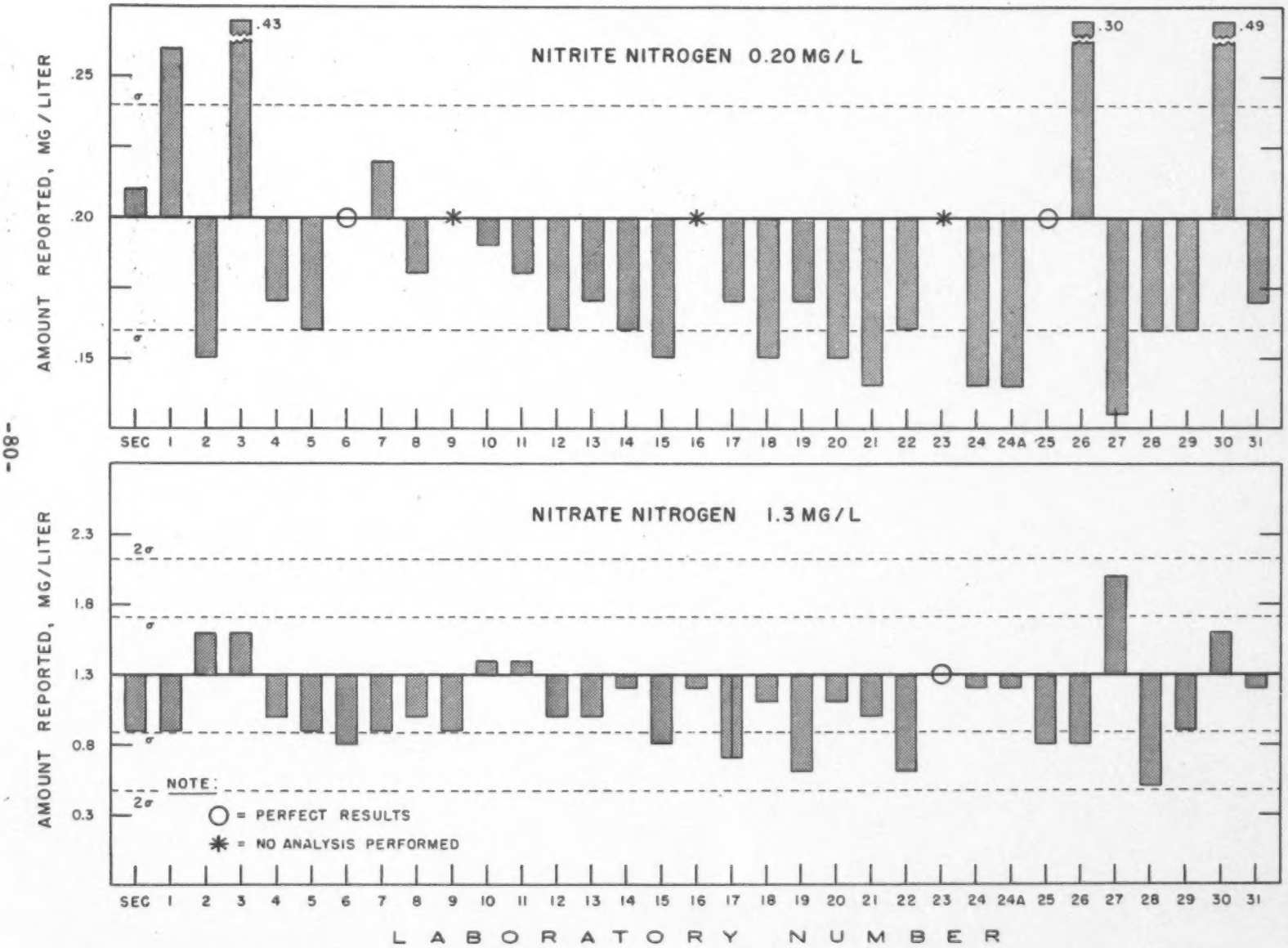


ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE I-A



ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE I-A


NITRITE NITROGEN 0.20 MG/L
AMOUNT REPORTED, MG/LITER
.25
.20
.15
σ
σ
.43
.30
.49
SEC 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 24A 25 26 27 28 29 30 31
NITRATE NITROGEN 1.3 MG/L
AMOUNT REPORTED, MG/LITER
2.3
1.8
1.3
0.8
0.3
2σ
σ
σ
2σ
NOTE:
○ = PERFECT RESULTS
✱ = NO ANALYSIS PERFORMED
SEC 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 24A 25 26 27 28 29 30 31
LABORATORY NUMBER

ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE I-A